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MOLECULAR CONSTANTS OF SULFUR DICHLORIDE FROM MICROWAVE SPECTRUM ANALYSIS

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TABLE OF CONTENTS

TABLE OF CONTENTS (Concluded)

LIST OF TABLES

SUMMARY

The purpose of this research was to investigate the microwave spectrum of sulfur dichloride; to determine the moments of inertia of the molecule, the structure of the molecule, and the electric dipole moment; to study the electric quadrupole coupling of the chlorine nuclei; and to attempt to ascertain to what extent the rigid rotor approximation is valid for this molecule.

Toward these ends measurements have been made on the microwave absorption spectrum of the most abundant isotopic species of the molecule, $S^{32}Cl_2^{35}$, in the region 9,000 to 36,000 Mc. The hyperfine splittings resulting from the electric quadrupole interactions of the chlorine nuclei have been measured in a majority of the rotational transitions studied, and measurements have been made on the Stark effect of the center component of the $0_o \rightarrow 1_o$ transition.

The resulting data have been analyzed to obtain the rotational constants, the structure, the quadrupole coupling constants, and the electric dipole moment. These results are given below.

Rotational Constants: A = 14613.3 Mc, B = 2920.86 Mc, C = 2430.69 Mc

Asymmetry Parameter: $\kappa = - 0.919530$

Effective Structure: $r = 2.014 \pm 0.004$A, $\theta = 102.8° \pm 0.2°$

Quadrupole Coupling Constants: $\chi_{aa} = - 38.81$ Mc, $\chi_{bb} = - 8.93$ Mc, $\chi_{cc} = 47.74$ Mc

Electric Dipole Moment: $\mu_b = 0.36 \pm 0.01$ Debye.

It has been found that the rigid rotor approximation is not good enough to predict the spectrum to within experimental errors; however, an insufficiency of high J data does not permit inclusion of centrifugal distortion effects.

CHAPTER I

INTRODUCTION

A systematic study of the absorption spectrum of a molecule in the microwave region can yield much information concerning the structure of the molecule. Such spectra are mainly the result of electric dipole transitions between rotational states of the molecule; and since the principal moments of inertia govern the rotational dynamics of any body, an accurate measurement of these transition frequencies may be used to obtain the principal moments of inertia of the molecular framework. In many cases enough data can be gathered to permit the determination of a complete structure of the molecule (1). Electric and magnetic multipole moments of the nuclei in the molecule frequently interact with charges in the molecule to produce a measurable splitting of the spectral lines. Most prominent in this respect is the splitting resulting from the electric quadrupole moments of nuclei of spin greater than one-half. This splitting depends upon the electric quadrupole moment of the nucleus, the average electric field gradient at the position of the nucleus, and the nuclear spin. Measurement of these splittings can then yield information about nuclear moments, nuclear spins, and molecular electronic wave functions. A further splitting results when the molecule is placed in an external electric field. This splitting, the Stark effect, is the result of the interaction of the external electric field and the permanent electric dipole moment of the molecule. A measurement of the split-

ting makes possible a determination of this dipole moment. Molecular rotational spectra can sometimes be treated by assuming that the molecule is an assemblage of masses connected by massless inextensible rods (the rigid rotor approximation). When transitions between high energy states are studied this approximation may become poor, and a more refined treatment may be necessary. Measurements of deviations from rigid rotor theory (centrifugal distortion effects) can in some cases lead to information concerning the interatomic potential function in the molecule (2).

The purpose of the work reported here is to investigate the microwave spectrum of sulfur dichloride and to determine the moments of inertia, the structure, the electric dipole moment, and the electric quadrupole coupling of the chlorine nuclei. An attempt is also made to ascertain to what extent the rigid rotor approximation is valid for this molecule.

Previous work on sulfur dichloride includes a determination of the molecular structure by electron diffraction techniques (3, 4), and studies of its infrared spectrum (5, 6). The results of the infrared work have been used to calculate the inertial defect of the molecule (7).

There appears to be no previously published work on the microwave spectrum of the molecule and no determination of either its electric dipole moment or the quadrupole coupling.

CHAPTER II

EXPERIMENTAL APPARATUS AND TECHNIQUES

Apparatus

The observation and measurement of the microwave spectrum of sulfur dichloride which is described in this report was carried out using a conventional Stark-modulated microwave spectrograph of the type first described by Hughes and Wilson (8). A detailed description of the particular instrument used in this investigation has previously been given by Clayton (9), and it will, therefore, be described only briefly here.

This spectrograph consists of four major components. A reflex klystron supplies microwave energy of variable frequency to one end of an absorption cell which contains the gas being studied. After passing through the gas in the absorption cell, the microwave energy is received by a complex of electronic devices which comprize the detection apparatus. The remaining major component is an assemblage of instruments forming the frequency measurement device.

The klystrons used are those of the Varian X and Raytheon QK series. The associated power supplies are commercial units.

The absorption cell is a seventeen-foot section of brass X-band wave guide which is sealed at both ends by Mylar windows of three mil thickness. The gas to be studied is admitted to the cell via a narrow slot a few inches in length located on one broad face of the cell near one end.

A brass strip Stark-electrode is suspended in the center of the absorption cell. It is held in place and insulated from the body of the cell by slotted Teflon strips. A voltage applied between this Stark-electrode and the wave guide produces an electric field which is parallel to the electric field of the microwave radiation. In practice, this Stark field is supplied by application of the output of an eighty-five kilocycle square wave generator (10, 11, 12) between the Stark electrode and the wave guide. One side of this square wave is clamped to ground potential and the amplitude is continuously variable from zero to - 1,000 volts. As a result of this eighty-five kilocycle electric field, the microwave power is amplitude modulated as the klystron output frequency is swept over an absorption line. This amplitude modulated signal is detected by a silicon diode and is then amplified by a narrow band eighty-five kilocycle amplifier. The output of this amplifier passes into a phase sensitive detector which uses a signal from the square wave generator as its reference. The output of the phase sensitive detector may be displayed either on an oscilloscope which is swept by the same oscillator which sweeps the klystron or on an Esterline-Angus recording milliammeter. The latter display affords greater sensitivity by allowing the use of long time constants in the output circuits of the phase sensitive detector.

The frequencies of rotational lines are measured by a method similar to that described by Unterberger and Smith (13). Vacuum tube circuitry is employed to multiply the output of a five megacycle crystal oscillator to obtain harmonics at 30, 90, 270, 540, 1080, and 2160 megacycles. These harmonics are applied to a crystal diode in the wave guide and are thereby multiplied into the microwave region. The result is a

series of standard frequencies 30 megacycles apart in the microwave region. The frequency of the five megacycle oscillator is periodically compared with the frequency of the ten megacycle broadcasts of the National Bureau of Standards Station WWV to maintain the accuracy necessary for these precise measurements. Some of the energy from the klystron is also applied to the crystal diode which mixes it with the standard harmonics. The resulting beat note in the 15 to 30 megacycle region is measured on a calibrated HRO "Sixty" communications receiver. Knowledge of the frequency of the harmonic which produces the beat then yields the absorption frequency. Harmonics are identified by approximate frequency measurements made with an absorption wave meter, and the identification is sometimes facilitated by turning off all multiples of 30 megacycles leaving only multiples of 90 megacycles.

Sample Preparation

The sulfur dichloride used in this investigation was supplied by the Hooker Chemical Corporation. As received, it contained sufficient chlorine gas to cause difficulty in obtaining large enough vapor pressure of sulfur dichloride for spectrum observation at Dry Ice temperatures. Accordingly the sample was purified before use by pumping on it at Dry Ice temperature until the volume was reduced approximately fifty percent. The remaining fraction was stored at Dry Ice temperature and used for the experimental observations.

Spectrum Observation and Measurement

In order to increase the population of the ground vibrational state and to a certain extent the low J rotational states, the absorption cell was cooled with Dry Ice to - 80° C. At this temperature sulfur dichloride appears to condense rapidly on the walls of the cell. Attempts to continuously pump it through the cell to reduce the concentration of contaminants resulting from its reaction with the brass wave guide were frustrated by a shorting of the Stark field through the condensed sulfur dichloride. The procedure adopted in this investigation was to admit as much sample to the cell as was possible without a breakdown of the Stark field. When the spectrum became weak due to decomposition of the sulfur dichloride, the cell was pumped clean and a fresh sample was admitted. The resulting vapor pressure in the absorption cell was generally less than 20 microns.

As the spectrum of sulfur dichloride observed under the above described conditions is rather weak, only the strongest lines could be measured using the oscilloscope display described by Clayton (14). Most measurements of hyperfine lines, all Stark lines, and several rotational lines were made using the recorder display scheme and a nearby strong line which could be measured using the oscilloscope display. This strong line was sometimes of unknown origin resulting from an unidentified transition in one of the isotopic species of sulfur dichloride or in SO_2 which was known to be an impurity present in the absorption cell or, perhaps, in some other impurity. More often it was one of the lines in the group being measured. These measurements were made by a method first described by Wolfe (15) in which the output of the harmonic generator and also the

output of the five megacycle crystal oscillator are impressed upon the multiplying crystal. This produces harmonics five megacycles apart in the microwave region. The klystron output is mixed with these harmonics in the standard fashion, and beat notes are then received on two calibrated communications receivers set at 25.625 megacycles and 26.875 megacycles. As the klystron is mechanically driven slowly across a group of lines, the operator listens to the audio outputs of the two receivers and makes a mark on the strip chart by means of a relay actuated marking pen when a beat note is heard. The resulting marks are spaced every 1.25 megacycles on the strip chart, and linear interpolation is used to determine the splittings of the individual lines from a single strong line which has been measured by the oscilloscope display technique. An average of the results of ten such measurements was in most cases adopted as the measured value of the splitting.

CHAPTER III

THEORETICAL BACKGROUND

It is intended to present in this chapter those results of numerous theoretical investigations of other authors which are useful in the interpretation of the microwave spectrum of an asymmetric rotor containing two nuclei of spin greater than one-half. The treatments given are brief and not necessarily complete. The reader who desires a complete treatment is referred to the original literature as cited throughout.

The Rigid Asymmetric Rotor

The quantum mechanical treatment of the rigid asymmetric rotor has been given in several equivalent forms by many authors. The discussion which is given below is essentially that of Cross, Hainer and King (16) who have gathered the bits and pieces of the treatment from the various authors and have given a prescription for computation of the essential features of rigid asymmetric rotor spectra.

Energy Eigenvalues

The Hamiltonian of a rigid asymmetric rotor is

$$H = \left[\frac{P_a^2}{2I_a} + \frac{P_b^2}{2I_b} + \frac{P_c^2}{2I_c} \right] \qquad (1)$$

where $I_a \leq I_b \leq I_c$ are the principal moments of inertia of the molecule and P_a, P_b, and P_c are components of the total rotational angular momentum along the principal inertial axes of the molecule. It is convenient to define rotational constants A, B, and C by

$$A = \hbar^2/2I_a,\ B = \hbar^2/2I_b,\ C = \hbar^2/2I_c \tag{2}$$

where $\hbar$ is Planck's constant divided by 2π. In terms of these constants the Hamiltonian becomes:

$$H = (AP_a^{\,2} + BP_b^{\,2} + CP_c^{\,2})/\hbar^2 \tag{3}$$

The operators P_a, P_b, and P_c must satisfy the commutation relations

$$\left[P_a,\ P_b\right] = -\,i\hbar P_c,\ \text{cyclic} \tag{4}$$

as has been shown by Klein (17).

The eigenvalues of H can be determined by calculating the matrix elements of H in any convenient basis and diagonalizing the resulting matrix by means of a similarity transformation. One such convenient basis is a symmetric rotor basis in which the square of the total angular momentum and the component along the a - axis are diagonal. That is

$$P^2 \mid JK) = \hbar^2\, J(J+1) \mid JK) \tag{5}$$

and

$$P_a \mid JK) = \hbar K \mid JK),\ \mid K \mid \leq J$$

These relations, which define the basis set, and the commutation relations, Equation (4), can then be used to calculate the nonvanishing matrix elements of P_b and P_c. These are

$$(JK \mid P_b \mid JK+1) = i(JK \mid P_c \mid JK+1) = i\frac{\hbar}{2}[J(J+1) - K(K+1)]^{\frac{1}{2}} \quad (6)$$

and

$$(JK+1 \mid P_b \mid JK) = -i(JK+1 \mid P_c \mid JK) = -i\frac{\hbar}{2}[J(J+1) - K(K+1)]^{\frac{1}{2}}$$

The phase has been chosen such that P_c is real and positive while P_b is imaginary.

The Hamiltonian contains the squares of these matrices, however. A straight forward matrix multiplication yields for the nonvanishing components of these squares

$$(JK \mid P_c^2 \mid JK) = (JK \mid P_b^2 \mid JK) = \frac{\hbar^2}{2}[J(J+1) - K^2] \quad (7)$$

$$(JK \mid P_c^2 \mid JK+2) = -(JK \mid P_b^2 \mid JK+2) =$$

$$\frac{\hbar^2}{4}\left\{[J(J+1) - K(K+1)][J(J+1) - (K+1)(K+2)]\right\}^{\frac{1}{2}}$$

and $(JK \mid P_a^2 \mid JK) = \hbar^2 K^2$

It is convenient to rewrite the Hamiltonian (3) in terms of an asymmetry parameter introduced first by Ray (18). This parameter, which is conventionally called "Kappa," is defined by

$$\kappa = (2B - A - C)/(A - C) \tag{8}$$

The simplest way to introduce this parameter in this treatment is to write the Hamiltonian in the form

$$\begin{aligned} H &= (1/2\hbar^2)\Big\{(A + C)\left[P_a^{\,2} + P_b^{\,2} + P_c^{\,2}\right] \\ &\quad + (A - C)\left[P_a^{\,2} + \frac{2B - A - C}{A - C} P_b^{\,2} - P_c^{\,2}\right]\Big\} \\ &= \left[(1/2)(A + C)\, P^2 + (1/2)(A - C)H'\right]/\hbar^2 \end{aligned} \tag{9}$$

where $$H' = P_a^{\,2} + \frac{2B - A - C}{A - C} P_b^{\,2} - P_c^{\,2}$$

and H' is called the reduced Hamiltonian.

The term $(A + C)\, P^2/2\hbar^2$ is diagonal in the representation chosen here but the reduced energy matrix must be diagonalized.

Using the matrix elements of $P_a^{\,2}$, $P_b^{\,2}$, and $P_c^{\,2}$ the matrix elements of H' are found to be

$$(K \mid H' \mid K) = (1/2)(\kappa - 1)J(J + 1) + (1/2)(3 - \kappa)K^2 \tag{10}$$

and

$$\begin{aligned} (K \mid H' \mid K + 2) &= (K + 2 \mid H' \mid K) \\ &= -(1/2)(\kappa + 1)\Big\{\left[J(J + 1)/4 - K(K + 1)\right]\left[J(J + 1) - (K + 1)(K + 2)\right]\Big\}^{\frac{1}{2}} \\ &= -(1/2)(\kappa + 1)\left[f(J, K + 1)\right]^{\frac{1}{2}} \end{aligned}$$

where the last equality defines $f(J, K + 1)$.

The quantum number J has been dropped in the matrix notation since the reduced Hamiltonian is diagonal in J.

For each value of J this matrix can be written as the direct sum of not more than four submatrices by application of a simple similarity transformation (19). These submatrices, called $E^{\pm}$ and $O^{\pm}$, may then be displayed in the forms

$$E^{\pm} = \begin{vmatrix} E_{00} & 2^{\frac{1}{2}}E_{02} & 0 & \cdots \\ 2^{\frac{1}{2}}E_{02} & E_{22} & E_{24} & \cdots \\ 0 & E_{24} & E_{44} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{vmatrix} \tag{11}$$

and

$$O^{\pm} = \begin{vmatrix} (E_{11} \pm E_{-11}) & E_{13} & 0 & \cdots \\ E_{13} & E_{33} & E_{35} & \cdots \\ 0 & E_{35} & E_{55} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{vmatrix}$$

where E^{-} has the same elements as E^{+} after removal of the first row and the first column and $E_{ij} = (i \mid H' \mid j)$. Using the matrix elements given by Equation (10), these matrices can be written as

$$E^{\pm} = \begin{vmatrix} FJ(J+1) & H[2f(J,1)]^{\frac{1}{2}} & 0 & \cdots \\ H[2f(J,1)]^{\frac{1}{2}} & FJ(J+1)+4G & H[f(J,3)]^{\frac{1}{2}} & \cdots \\ 0 & H[f(J,3)]^{\frac{1}{2}} & FJ(J+1)+16G & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{vmatrix} \tag{12}$$

and

$$O^{\pm} = \begin{vmatrix} FJ(J+1) + G \pm H[f(J,0)]^{\frac{1}{2}} & H[f(J,2)]^{\frac{1}{2}} & 0 \\ H[f(J,2)]^{\frac{1}{2}} & FJ(J+1)+9G & H[f(J,4)]^{\frac{1}{2}} \\ 0 & H[f(J,4)]^{\frac{1}{2}} & FJ(J+1)+25G \\ \cdots & \cdots & \cdots \end{vmatrix}$$

where $H = -\frac{1}{2}(\kappa + 1)$

$G = -\frac{1}{2}(\kappa - 3)$

and $F = \frac{1}{2}(\kappa - 1)$

Eigenvalues of these matrices have recently been tabulated as a function of κ in steps of 0.001 from $\kappa = -1$ to $\kappa = +1$ for $J \leq 16$ by Nolan, Sidran, and Blaker (20, 21, 22, 23, 24). Erlandsson (25) has tabulated them in steps of 0.10 through $J = 40$. Previous tabulations are those of Cross, Hainer, and King (26) and Turner, Hicks, and Reitwiesner (27).

For $J \leq 3$ and certain matrices for $J = 4, 5$ the resulting secular equations are of order two or less, and these have been solved in closed form (28). For cubic and higher order secular equations, closed form solutions are either cumbersome or unknown. These eigenvalues are obtained by numerical diagonalization of the matrices.

The factoring of the matrices into four submatrices has several advantages. Since the resulting submatrices are of lower order than the initial matrix, the computation of eigenvalues can be accomplished more rapidly. Of primary importance, however, is the fact that the wave functions for all states of a given submatrix belong to a particular one of

the four irreducible representations of the Four-group.* This fact is useful in determining selection rules; therefore, the species of the four submatrices are given in Table 1.

The energy eigenvalues are labeled in the following manner. The value of the quantum number J is given. To distinguish between the 2J + 1 sublevels associated with a given value of J, a subscript, τ, is placed after the value of J. The sublevel with the largest energy is identified by τ = J, the next largest by τ = J - 1, and so on to the smallest which is identified by τ = - J.

An alternate method which is more convenient than the above for specifying selection rules has been proposed by Cross, Hainer, and King (29). This method uses two subscripts after J. The first, K_{-1}, takes the values 0, 1, 1, 2, 2,... from lowest to highest energy values; and the second, K_1, takes the values 0, 1, 1, 2, 2,... from highest to lowest energy values**. The subscript, τ, is given in terms of these two subscripts by

$$\tau = K_{-1} - K_1 \tag{13}$$

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*The Four-group is the group of operations E, C_2^a, C_2^b, and C_2^c under which the asymmetric rotor Hamiltonian is invarient. The four irreducible representations are A, B_a, B_b, and B_c.

**K_{-1} and K_1 are the magnitudes of the quantum number K which labels the limiting prolate and oblate symmetric rotor states respectively.

Table 1. Symmetry Classification of the Submatrices

Submatrix	Species Representation	
	J even	J odd
E^+	A	B_a
E^-	B_a	A
O^+	B_c	B_b
O^-	B_b	B_c

The convenience of this method arises from the fact that the species of the wave function for a state $|JK_{-1}K_1)$ is given by the evenness or oddness of the subscripts K_{-1} and K_1. If e indicates an even subscript and o an odd subscript, then the species A, B_a, B_b, and B_c are associated with the indices ee, oe, oo, eo respectively.

Selection Rules for Dipole Radiation

In the calculation of energy eigenvalues the molecule has been considered to be a rigid asymmetric rotator rotating about its center of mass. That is, the motion has been separated into motion of the center of mass and motion about the center of mass. Since the motion of the center of mass is constant in a field free region, it need not be considered. If the motion about the center of mass is considered in detail, one finds that there is one additional constant of the motion. This is P_z, the projection of the total angular momentum upon a space fixed z-axis. P_z has eigenvalues $M\hbar$, where $M = J, J - 1, J - 2, \ldots - J$.

Cross, Hainer and King have derived in detail the selection rules for J, M, and the symmetry species of an asymmetric rotor (30). They are given in Table 2.

The selection rule, $\Delta M = 0$ and ± 1 is meaningless in the field free case as the $2J + 1$ levels of different M are all degenerate. This selection rule will be of importance in later considerations. The selection rule $\Delta M = 0$ applies when the radiation emitted in the transition or inducing the transition is plane polarized with its $\underline{E}$ field parallel to the space fixed z-axis while $\Delta M = \pm 1$ applies to radiation polarized perpendicular to the z-axis.

Table 2. Asymmetric Rotor Selection Rules

Dipole Moment Component	Allowed Transitions
a	$A \longleftrightarrow B_a$ ee $\longleftrightarrow$ oe
	$B_b \longleftrightarrow B_c$ oo $\longleftrightarrow$ eo
b	$A \longleftrightarrow B_b$ ee $\longleftrightarrow$ oo
	$B_a \longleftrightarrow B_c$ oe $\longleftrightarrow$ eo
c	$A \longleftrightarrow B_c$ ee $\longleftrightarrow$ eo
	$B_a \longleftrightarrow B_b$ oe $\longleftrightarrow$ oo

In all cases $\Delta J = 0, \pm 1$; $\Delta M = 0, \pm 1$.

Electric Quadrupole Coupling of Two Identical Nuclei of Spin 3/2 in an Asymmetric Rotor

The problem of the interaction of nuclear electric quadrupole moments with molecular rotation has been treated in various cases by numerous authors. Early workers extended the atomic treatment of Casimir (31) to diatomic, linear polyatomic, and symmetric rotor molecules containing one or two quadrupolar nuclei. Bragg (32, 33) extended the theory to include asymmetric rotors containing one or two quadrupolar nuclei. Meyers and Gwinn (34) used the matrix elements given by Condon and Shortley (35) to obtain the Hamiltonian matrix for the first order perturbation treatment of two equivalent quadrupolar nuclei interacting with the molecular rotation. Robinson and Cornwell (36) presented the treatment for two identical or "nearly identical" nuclei of spin 3/2 and tabulated certain quantities which are useful in calculating the first order energy shifts in this case. The treatment described below is that of Robinson and Cornwell for identical nuclei.

The first-order interaction of nuclear electric quadrupole moments with the internal electric field of an atom or molecule is described by the Hamiltonian (37)

$$\sum_i \left[(eQ_i \langle (\partial^2 V/\partial Z^2)_i \rangle_{av})/2J(2J-1)(2I_i-1)I_i \right] \qquad (14)$$

$$\times \left[3(\underline{I}_i \cdot \underline{J})^2 + \tfrac{3}{2}(\underline{I}_i \cdot \underline{J}) - \underline{I}_i^{\,2}\, \underline{J}^2 \right]$$

where the sum extends over all quadrupolar nuclei in the system, $\underline{I}_i$ is

the nuclear spin angular momentum operator for the i^{th} nucleus, $\underline{J}$ is the rotational angular momentum operator for the system, Q_i is the quadrupole moment of the i^{th} nucleus defined by

$$eQ_i = \langle 3Z_i^2 - r_i^2 \rangle_{av} \tag{15}$$

where e is the electron charge, $\underline{r}_i$ locates nuclear charges with respect to an origin at the center of the i^{th} nucleus and the average is carried out over the nuclear charge distribution for nuclear state $M_{I_i} = I_i$, and finally,

$$\langle (\partial^2 V/\partial Z^2)_i \rangle_{av} = \int \rho_{e, M_J = J} \left[\frac{3Z^2_{e_i} - r^2_{e_i}}{r^5_{e_i}} \right] d\tau_e \tag{16}$$

where the integration is over the electron distribution, ρ_e, $\underline{r}_{e_i}$ is the vector locating the system charge ρ_e with respect to the origin at the center of the i^{th} nucleus, and V is the potential at the i^{th} nucleus resulting from all extranuclear charges (38).

The quantity eQ_i is a nuclear constant and the quantity $\langle (\partial^2 V/\partial Z^2)_i \rangle_{av}$ depends upon the rotational state of the system. This latter quantity has been evaluated for molecules in terms of the reduced energy eigenvalues and their derivatives by Bragg and Golden (39). Thus $\langle (\partial^2 V/\partial Z^2)_i \rangle_{av}$ is easily evaluated for a given state by using the tabulations of these eigenvalues which have been mentioned earlier. The result of Bragg and Golden can be expressed in the form

$$eQ_i \langle(\partial^2 V/\partial Z^2)i\rangle \text{ av} = (A_i/2)\left[J(J+1) + E_\tau^J(\kappa)\right. \tag{17}$$

$$\left. - (\kappa+1)(\partial E_\tau^J(\kappa)/\partial\kappa)\right] + B_i(\partial E_\tau^J(\kappa)/\partial\kappa)$$

$$+ (C_i/2)\left[J(J+1) - E_\tau^J(\kappa) + (\kappa-1)(\partial E_\tau^J(\kappa)/\partial\kappa)\right]$$

where A_i, B_i, and C_i are given by

$$A_i = \frac{2eQ_i}{(J+1)(2J+3)} \frac{\partial^2 V}{\partial a^2}$$

$$B_i = \frac{2eQ_i}{(J+1)(2J+3)} \frac{\partial^2 V}{\partial b^2}$$

$$C_i = \frac{2eQ_i}{(J+1)(2J+3)} \frac{\partial^2 V}{\partial c^2}$$

The symbols a, b, and c denote the principal inertial axes of the molecule, κ is Ray's asymmetry parameter defined in Equation (8), and $E_\tau^J(\kappa)$ is the eigenvalue of the reduced energy matrix which gives the energy of the rigid asymmetric rotor state $|\ J\ \tau)$. The quantity $eQ_i \langle(\partial^2 V/\partial Z^2)_i\rangle$ is hereinafter referred to as the coupling.

In the treatment of Robinson and Cornwell (40), the first-order energy shift, $\Delta E_{\epsilon JF}$, resulting from the interaction of two identical nuclei of spin 3/2 with the molecular rotation is expressed as

$$\Delta E_{\epsilon JF} = eQ_1 \left\langle (\partial^2 V / \partial Z^2)_1 \right\rangle_{av} \lambda_{\epsilon JF} \tag{18}$$

where $\lambda_{\epsilon JF}$ is an eigenvalue of the operator

$$\frac{\left\{ \left[3(\underline{I}_1 \cdot \underline{J})^2 + \frac{3}{2}(\underline{I}_1 \cdot \underline{J}) - \underline{I}_1^2 \underline{J}^2 \right] + \left[3(\underline{I}_2 \cdot \underline{J})^2 + \frac{3}{2}(\underline{I}_2 \cdot \underline{J}) - \underline{I}_2^2 \underline{J}^2 \right] \right\}}{2J(2J - 1)I(2I - 1)}$$

J is the rotational angular momentum quantum number, F is a quantum number specifying the eigenvalue of the operator $\underline{F}^2 = (\underline{I}_1 + \underline{I}_2 + \underline{J})^2$ with $\underline{I}_1 + \underline{I}_2 = \underline{I}$. The subscript ϵ is a pseudospin quantum number which labels the states in a fashion similar to that in which τ labels the rotational states. The quantum number F assumes the values $| J + \epsilon |$, $|J + \epsilon - 1 |$, ..., $|J - \epsilon |$. The states of odd ϵ are symmetric under interchange of the two identical nuclei while those of even ϵ are antisymmetric under such an interchange.

Thus, in this case, the first-order energy shifts for a state $| J \tau)$ are known as soon as the coupling is evaluated for that state. As suggested by Bragg and Golden (41), Equation (17) can be simplified by using $\nabla^2 V = 0$. The coupling then becomes

$$\chi^+ = eQ_1 \left\langle (\partial^2 V / \partial Z^2)_1 \right\rangle_{av} = \frac{J}{2J + 3} \left[\chi_+ A(J,\tau) + \chi_- B(J,\tau) \right] \tag{19}$$

where

$$\chi_\pm = eQ_1 \left[(\partial^2 V / \partial a^2) \pm (\partial^2 V / \partial c^2) \right]$$

$$A(J,\tau) = \left[1 - \frac{3}{J(J+1)} \frac{\partial E_\tau^J(\kappa)}{\partial \kappa}\right]$$

and

$$B(J,\tau) = \frac{1}{J(J+1)} \left[E_\tau^J(\kappa) - \kappa \frac{\partial E_\tau^J(\kappa)}{\partial \kappa}\right]$$

In calculating the effect the nuclear quadrupole coupling has upon the observed rotational spectrum, one must be sure to consider the effect of the identical nature of the two quadrupolar nuclei. Since for nuclear spin 3/2 the nuclei are Fermions, the total molecular wave function must be antisymmetric under any operation which permutes these two particles. Thus, for a molecule such as sulfur dichloride, in which the intermediate principal inertial axis is a C_2 axis of symmetry, the total wave function must be antisymmetric under the operation C_2^b. Then for a totally symmetric electronic-vibrational state, only symmetric nuclear states exist for antisymmetric rotational states; and, conversely, only antisymmetric nuclear states exist for symmetric rotational states. For a given value of J, the substates with even τ are symmetric under the operation C_2^b while those of odd τ are antisymmetric. Thus for even τ only those nuclear states with $\epsilon = 0,2$ exist while for odd τ only those nuclear states with $\epsilon = 1,3$ exist. Except for $J \leq 2$ there are ten nuclear states with $\epsilon = 1,3$ while there are only six with $\epsilon = 0,2$. Furthermore, for $\epsilon = 0,2$ four of these states are degenerate with $\lambda_{\epsilon JF} \equiv 0$ while the λs for the other two differ only in sign. If the molecule does not have this C_2 symmetry or if the two quadrupolar nuclei are not identical, then for every τ all sixteen states exist. Thus, the energy level pattern is greatly

simplified by the restrictions imposed by the identical nature of the two quadrupolar nuclei.

As one might expect, the spectrum is also greatly simplified. The molecule can have a dipole moment only along the C_2 axis, in the case of SCl_2^{35} the b axis. Then for SCl_2^{35}, inspection of Table 2 shows that rotational transitions are allowed from states of even τ to states of even τ only and from states of odd τ to states of odd τ only. The transitions between states of even τ then appear as symmetric patterns of not more than nine lines. The center line is approximately four times as strong as the strongest of the remaining eight and has the frequency of the rigid rotor line neglecting the quadrupolar nuclei. The transitions between states of odd τ appear as unsymmetric groups of lines of varying intensity none of which has the frequency of the unperturbed rigid rotor line. Thus, when two quadrupolar nuclei are present, the case where they are identical presents the easiest situation so far as interpretation of the spectrum is concerned. Still, although there are many molecules of this type and the theory has been available for some ten years, a relatively small number of such molecules have been studied.

The tables of line strengths and the tabulation of $\lambda_{\epsilon JF}$ given by Robinson and Cornwell (42) are useful in the calculation of these so-called hyperfine splittings which result from two identical nuclei of spin 3/2. The latter table gives $\lambda_{\epsilon JF}$ only for $J \leq 12$. It has been extended to $J = 40$ by the present author. This extended table will be found in Appendix C.

Stark Effect of a Near Prolate Asymmetric Rotor Containing Two Identical Quadrupolar Nuclei of Spin 3/2

The theory of the Stark effect of a rigid asymmetric rotor has been considered by several authors. Golden and Wilson (43) developed the theory for molecules containing no quadrupolar nuclei, and considered the possibility of accidental near-degeneracy of rotational energy levels. Mizushima (44) considered the problem of the Stark effect of molecules containing a quadrupolar nucleus. He did not consider the case in which pairs of rotational levels are near-degenerate. A treatment of most general validity has recently been given by Eagle (45) in which the Stark and quadrupole perturbation Hamiltonians are treated simultaneously and the energy level shifts are obtained to second order. The difficulties arising from the possibility of accidental near-degeneracy of pairs of rotational levels are explicitly treated in this work. Although Eagle's paper specifically describes only the case of a molecule containing one quadrupolar nucleus, this limitation in unnecessary in his treatment. His results, therefore, hold for any number of quadrupolar nuclei in an asymmetric rotor. It is the purpose of this section to indicate Eagle's results and to apply them to the specific problem of calculation of the Stark effect of the $0_o \rightarrow 1_o$ transition in a molecule such as SCl_2^{35}, which is a near prolate asymmetric rotor of C_{2v} symmetry in which two identical Fermions are interchanged by the operation C_2^b.

The Hamiltonian of a molecule, with a permanent electric dipole moment $\underline{\mu}$ and containing quadrupolar nuclei, located in an external electric field is

$$H = H^R + EH^S + H^Q \tag{20}$$

where H^R is the rotation Hamiltonian treated earlier, EH^S is the Hamiltonian for the interaction of the electric dipole moment, $\underline{\mu}$, with the electric field, $\underline{E}$, and H^Q is the Hamiltonian for the interaction of the nuclear electric quadrupole moments with the electric field gradients. The rotation, vibration, and electronic energies are assumed here to be separable and the latter two are neglected since they do not change in the transitions considered.

The Stark effect Hamiltonian, EH^S, may be written

$$EH^S = E \sum_{g=1}^{3} \mu_g \cos \alpha_{Zg} \tag{21}$$

where E is the magnitude of the external electric field, μ_g is the component of the dipole moment along the g^{th} principal axis and α_{Zg} is the angle between $\underline{E}$ and the g^{th} principal axis.

The quadrupole Hamiltonian may be expressed as a sum over all quadrupolar nuclei in the molecule as

$$H^Q = \sum_{i=1}^{N} H^{Q_i} \tag{22}$$

where H^{Q_i} is the quadrupole interaction Hamiltonian for the i^{th} quadrupolar nucleus in the molecule. It may be of the form used earlier in this chapter in connection with the first-order treatment of the quadru-

pole interaction alone or it may be of the more general form given by Bragg (46). The particular form indicated by the symbol is unimportant at present, and unless it is explicitly stated to the contrary it may be assumed that the general expression is meant in what follows.

Eagle's theory treats the latter two Hamiltonians, EH^S and H^Q, simultaneously as perturbations upon the former. He calculates that, to second order, the Hamiltonian is the following (47)

$$\text{Zeroth order:} \quad H^o_{ij} = W^o_i \, \delta_{ij} + H^Q_{ij} \tag{23}$$

$$\text{First order :} \quad H^1_{ii} = 2E \sum_k{}' \frac{H^S_{ik} H^Q_{ki}}{W^o_i - W^o_k}$$

$$H^1_{ij} = EH^S_{ij} + E \sum_k{}' \left[\frac{H^S_{ik} H^Q_{ij}}{W^o_i - W^o_k} - \frac{H^Q_{ik} H^S_{kj}}{W^o_k - W^o_j} \right],$$

$$i \neq j \qquad W^o_i \text{ near } W^o_j$$

$$= 0 \qquad i \neq j \qquad W^o_i \text{ not near } W^o_j$$

$$\text{Second order:} \quad H^2_{ii} = E^2 \sum_k{}' \frac{H^S_{ik} H^S_{ki}}{W^o_i - W^o_k}$$

where $$W^o_i = (i \mid H^R \mid i)$$

and $$H^{Q}_{ij} = (i \mid H^{Q} \mid j)$$

and the primes on the sums indicate that the sum extends over all states except those which cause a denominator to be near zero.

Diagonalization of the above Hamiltonian matrix then gives the perturbed energies of the molecule correct to second order.

Except for the prime on the sum, the second-order Hamiltonian is the same as the one obtained by Golden and Wilson (48) in their treatment of the Stark effect alone. Therefore, these diagonal elements may be written as

$$(J\tau M_J \mid H^2_g \mid J\tau M_J) = \mu^2_g E^2 \left\{ \frac{J^2 - M^2_J}{J(4J^2 - 1)} \sum_{\tau'}{}' \frac{\lambda_g(J\tau;\ J-1\ \tau')}{W^o(J\tau) - W^o(J-1\ \tau')} \right. \quad (24)$$

$$+ \frac{M_J^2}{J(J+1)(2J+1)} \sum_{\tau' \neq \tau}{}' \frac{\lambda_g(J\tau;\ J\tau')}{W^o(J\tau) - W^o(J\tau')}$$

$$\left. + \frac{(J+1)^2 - M_J^2}{(J+1)(2J+1)(2J+3)} \sum_{\tau'}{}' \frac{\lambda_g(J\tau;\ J+1\ \tau')}{W^o(J\tau) - W^o(J+1\ \tau')} \right\}$$

There is a term of the above type for each non-vanishing component of electric dipole moment, μ_g. The quantities $\lambda_g(J\tau;\ J'\tau')$ are the asymmetric rotor line strengths which have been tabulated by Cross, Hainer, and King (49) and by Schwendeman and Laurie (50). Closed form expressions for certain low J states have been given by Gora (51).

The above theoretical expressions are now applied to the calculation of the Stark effect of the center component of the $0_0 \longrightarrow 1_0$ triplet of SCl_2^{35}. There are no near degeneracies between rotational states for $J \geq 2$. Thus, the primes may be dropped from all sums, and the first-order off-diagonal matrix elements of H vanish.

Since it has been found that the first-order quadrupole theory presented earlier in this chapter is adequate to treat the quadrupole interaction in SCl_2^{35} (see Chapter IV), it may safely be assumed that matrix elements of H^Q off-diagonal in J and τ may be assumed to be zero. Thus, the first-order quadrupole Hamiltonian is used below. For the matrix element $(00 \mid H^1 \mid 00)$ the sum reduces to a single term since $H^S_{ik} = 0$ except for $(00 \mid H^S \mid 10)$. Since $(10 \mid H^Q \mid 00)$ is off-diagonal in J, it is assumed that it vanishes so that $(00 \mid H^1 \mid 00) = 0$. A similar argument shows that $(10 \mid H^1 \mid 10) = 0$. The first-order portion of H then vanishes. This leaves only the zeroth and second-order parts, and the second-order part is the same as one would have if there were no quadrupole interaction.

The second-order Stark effect matrix elements appearing in Equation (23) have been calculated in the rigid asymmetric rotor basis. Thus a basis including this as a subset will be appropriate for calculating the matrix elements of H^Q. The $J\ \tau\ M_J\ I_1\ I_2\ M_{I_1}\ M_{I_2}$ basis is chosen here. The additional quantum numbers I_1 and I_2 represent the nuclear spins of the two quadrupolar nuclei while the quantum numbers M_{I_1} and M_{I_2} represent the projection of these spins on a space-fixed z-axis. The Stark effect Hamiltonian does not depend on these operators so the matrix

elements of Equation (23) are unchanged.

Since the rotational wave function for both the states 0_o and 1_o is symmetric under the operation C_2^b which interchanges the two identical chlorine nuclei, only antisymmetric nuclear states are allowed. Symmetric and antisymmetric nuclear states are constructed by forming the appropriate linear combinations of unsymmetric states.

Symmetric

$$\frac{1}{\sqrt{2}}\left[|M_J\ M_{I_1}\ M_{I_2}) + |\ M_J\ M_{I_2}\ M_{I_1})\right]\ ;\ \text{for } M_{I_1} \neq M_{I_2} \qquad (25)$$

$$|\ M_J\ M_{I_1}\ M_{I_2})\ ;\ \text{for } M_{I_1} = M_{I_2}$$

Antisymmetric

$$\frac{1}{\sqrt{2}}\left[|\ M_J\ M_{I_1}\ M_{I_2}) - |\ M_J\ M_{I_2}\ M_{I_1})\ \right]$$

Matrix elements of the operator

$$\bigcirc = 3\left[(\underline{I}_1\cdot\underline{J})^2 + (\underline{I}_2\cdot\underline{J})^2\ \right] + \frac{3}{2}\left[(\underline{I}_1\cdot\underline{J}) + (\underline{I}_2\cdot\underline{J})\ \right] - I_1^2J^2 - I_2^2J^2 \qquad (26)$$

are then needed in the $J\ \tau\ M_J\ I_1\ I_2\ M_{I_1}\ M_{I_2}$ basis. Since $\bigcirc$ is invariant under any operator which interchanges particles 1 and 2, matrix elements of $\bigcirc$ between any symmetric and any antisymmetric state vanish. Thus, the symmetric states may be ignored. Matrix elements of an operator

$$3(\underline{I}\cdot\underline{J})^2 + \frac{3}{2}(\underline{I}\cdot\underline{J}) - I^2J^2$$

in the M_J, M_I basis have been given by Kellogg et al. (52), and their results may be used here. There will be a matrix for each value of the projection on the spaced-fixed z-axis of the total angular momentum $\underline{F}$. That is, the matrix is diagonal in F and M_F and is the direct sum of submatrices labeled by M_F. These submatrices are diagonal in J, τ, I_1, and I_2 but have off-diagonal elements in M_J, M_{I_1}, and M_{I_2}.

A matrix which gives the energy of the center level of the 1_o triplet is the $M_F = 2$ matrix. It is easy to show using Kellogg's matrix elements that this matrix is identically zero. Thus, the Hamiltonian matrix for this state is diagonal to the degree of approximation considered and has diagonal elements

$$W^o(1, 0) + (10\ M_J \mid H^2 \mid 10\ M_J) \tag{27}$$

The selection rule for M_J in a Stark modulated spectrograph with $\underline{E}$ field parallel to the electric field of the microwave energy is

$$\Delta M_J = 0 \tag{28}$$

Since for J = 0 there is only one value of M_J, $M_J = 0$, only the matrix element of H^2 with $M_J = 0$ need be considered in a calculation of the Stark effect of the $0_o \rightarrow 1_o$ transition.

The quadrupole Hamiltonian is identically zero for J = 0 so that

the frequency shift of the center component of the $0_o \rightarrow 1_o$ transition resulting from the Stark effect is given by

$$\Delta \nu_S = \left[W(1,\ 0,\ 0) - W(0,\ 0,\ 0) \right] - \nu^o(00;\ 10) \tag{29}$$

$$= \left[W^o(1,\ 0) + (100 \mid H^2 \mid 100) \right.$$

$$\left. - W^o(0,\ 0) - (000 \mid H^2 \mid 000) \right]$$

$$- \nu^o(00;\ 10)$$

where

$$\nu^o(00;\ 10) = W^o(1,\ 0) - W^o(0,\ 0) \tag{30}$$

is the line frequency without Stark effect. Therefore it follows that

$$\Delta \nu_S = (100 \mid H^2 \mid 100) - (000 \mid H^2 \mid 000) \tag{31}$$

where the matrix elements are to be evaluated using Equation (24). This Stark effect is unaffected by the quadrupole Hamiltonian.

CHAPTER IV

SPECTRUM ANALYSIS

In this chapter the theoretical results presented in Chapter III are applied to the analysis of the measured microwave spectrum of sulfur dichloride. The spectrum is given in Appendix B. The computer programs and numerical techniques used in the actual reduction of data are presented in Appendix A. All computer calculations were performed on the Burroughs 5000 at the Rich Electronic Computer Center.

Rotational Spectrum and Rotational Constants

In order to facilitate identification of the observed spectral lines of sulfur dichloride an approximate spectrum was calculated based upon the structural parameters obtained by Stevenson and Beach (53) through the use of electron diffraction techniques. According to their structure sulfur dichloride is a non-linear planar molecule in which two chlorine atoms are bonded to a single sulfur atom. The S-Cl distance was found to be 2.00 ± 0.02 A with a Cl-S-Cl angle of 103° ± 2°. Calculations based on this structure indicated that the principal inertial axis which passes through the sulfur atom and between the two chlorine atoms is the b-axis, the axis of intermediate moment of inertia. The approximate spectrum was seen to consist mainly of a Q-branch of the type $J_{-J} \rightarrow J_{-J+2}$. Of course, other lines were predicted, but they were considerably weaker. Qualitative considerations of the quadrupole

interaction indicated that the members of this Q-branch having even J should appear as symmetric groups of lines for the isotopic species of sulfur dichloride containing identical chlorine atoms and that those members having odd J should be unsymmetrical groups of lines. A preliminary search in the region 12,000 to 13,500 megacycles revealed the three lowest members of this group of transitions for the most abundant isotopic species, $S^{32}Cl_2^{35}$. The qualitative nature of the hyperfine splittings and the relative intensities of the groups appeared to be in agreement with what was expected. Subsequently this Q-branch assignment was completed through J = 8; but, as is well known, the Q-branch is not sufficient for obtaining complete information about rotational constants. The P and R-branch transitions were considerably weaker, and several early assignments proved to be incorrect. Finally, a correct R-branch assignment was made by calculating an approximate spectrum based upon the Q-branch assignment and the inertial defect calculated by Oka and Morino (54). A total of 17 rotational transitions were finally measured for the most abundant isotopic species of sulfur dichloride. The weakness of the spectra of the other isotopic species prevented measurements from being made on them.

The rotational constants were obtained by a least squares analysis of the seven measured rotational transitions of the symmetrical type for $J \leq 4$ utilizing the method described in Appendix A. These lines are members of P, Q, and R-branches; and as has been shown in Chapter III, they are unaffected by the quadrupole interaction. The results of this fitting are given in Table 3.

Table 3. Results of Fitting Rotational Constants to Seven Low J Rotational Transitions in $S^{32}Cl_2{}^{35}$*†

Transition $J_\tau \rightarrow J'_{\tau'}$	Measured Frequency ν_o^m (Mc)	Calculated Frequency ν_o^c (Mc)	$\nu_o^m - \nu_o^c$ (Mc)
$0_o \rightarrow 1_o$	17044.17	17044.01	0.16
$2_{-2} \rightarrow 2_o$	12687.96	12687.88	0.08
$2_{-2} \rightarrow 3_{-2}$	26527.85	26527.49	0.36
$3_{-2} \rightarrow 4_{-4}$	10722.4	10723.1	-0.7
$4_{-2} \rightarrow 3_o$	11995.8	11996.2	-0.4
$4_{-2} \rightarrow 4_o$	33615.96	33616.08	-0.12
$4_{-4} \rightarrow 4_{-2}$	14573.26	14573.14	0.12

*Average deviation between measured and calculated frequencies is -0.07 Mc. The Standard deviation is 0.45 Mc. A = 14613.32 Mc, B = 2920.861 Mc, and C = 2430.692 Mc.

†Estimated measurement error is indicated by number of figures carried. Where frequencies are given to tenths of a megacycle, the estimated error is ± 0.1 Mc. Where frequencies are given to hundredths of megacycles, the estimated error is ± 0.05 Mc.

The standard deviation of 0.45 Mc is rather large compared to the estimated uncertainty in the measured frequency of a line which is 0.10 Mc for the weakest lines and 0.05 Mc for the strongest. It is believed that these deviations result from the neglect of centrifugal distortion effects which have been seen to be appreciable in similar molecules even for such low values of J (55, 56, 57). These effects will be discussed further below.

The effective rotational constants and the resulting moments of inertia are given in Table 4.

The value of the inertial defect given in Table 4 is in agreement with the value 0.287 ± 0.060 amu A^2 calculated from the electron diffraction structure and the infrared spectrum by Oka and Morino (58).

The reasonableness of attributing the poor fit of Table 3 obtained using the rigid rotor approximation to centrifugal distortion effects has been tested by applying this approximation to the oxygen difluoride molecule. This molecule has a structure similar to that of sulfur dichloride and has been studied extensively in a non-rigid rotor approximation (59). The results of a rigid rotor analysis of its low-J spectrum which was measured by Pierce et al. (59) are given on page 92 These results are seen to be even worse than for sulfur dichloride. However, when Peirce et al. took the centrifugal distortion effects into account, these large deviations were eliminated. Thus, it seems reasonable to assume that the poor fit in the case of sulfur dichloride results from neglect of centrifugal distortion of the molecule.

Centrifugal distortion effects have also been taken into account for sulfur dioxide and ozone and have eliminated large deviations from

Table 4. Effective Rotational Constants and Moments of Inertia of $S^{32}Cl_2{}^{35}$*

Principal Axis	Rotational Constants	Moments of Inertia†
a	14613.3 Mc	34.5939 amu A^2
b	2920.86	173.0760
c	2430.69	207.9782

*$h/8\pi^2$ = 505531 Mc amu A^2

†$I_c - I_a - I_b$ = 0.308 amu A^2

the rigid rotor theory (59, 60, 61). In all three cases, however, transitions involving J values up to 38 were used. These transitions had large centrifugal distortion corrections.

Although no high J transitions have been measured in $S^{32}Cl_2{}^{35}$, an attempt has been made to include centrifugal distortion effects in the analysis of the rotational spectrum.

A Hamiltonian of the form (62)

$$H = \frac{1}{2} \sum_{\alpha,\beta} \sigma_{\alpha\beta} P_\alpha P_\beta + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \tau_{\alpha\beta\gamma\delta} P_\alpha P_\beta P_\gamma P_\delta$$

has been used. For a planar C_{2v} molecule such as $S^{32}Cl_2{}^{35}$ there are only seven nonvanishing τs and only four of these are independent (63). Furthermore, for such a molecule, only the diagonal σs are nonvanishing and they are essentially the effective rotational constants A, B, and C except for small centrifugal distortion corrections (64, 65).

Approximate values of these four independent τs may be calculated if the structure and the harmonic force constants of the molecule are known (66). These τs have been calculated for $S^{32}Cl_2{}^{35}$ using the approximate force constants given by Oka and Morino (67) and the electron diffraction structure of Stevenson and Beach (68). A spectrum was then calculated using these τs, the matrix elements of H given by Pierce, DiCianni, and Jackson (69), and the rotational constants of Table 4. The magnitude of the centrifugal distortion effects could then be calculated by comparison of this spectrum with one calculated on the basis of the rigid rotor theory. All lines measured were seen to be shifted by less

than three megacycles. The measured lines were corrected for these centrifugal distortion effects and the resulting spectrum was fitted by adjusting A, B, and C. The results are given in Table 5. The distortion constants T_i, i = 1, 2, . . ., 6 are those of Pierce, DiCianni, and Jackson (70) and are linear combinations of the four linearly independent τs.

The fit of Table 5 is readily seen to be better than that of Table 3 but it is still not satisfactory. An attempt was made to fit the entire observed rotational spectrum of $S^{32}Cl_2^{35}$ with rotational constants and centrifugal distortion constants simultaneously. The results were meaningless physically as an infrared frequency calculated from the distortion constants was not real. This lack of success is attributed to an insufficiency of high J data and to the small centrifugal distortion corrections to the low J transitions studied.

Molecular Structure

The molecular structure of a molecule as simple as sulfur dichloride can be obtained from a measurement of any two moments of inertia. The molecular structure may be specified by giving the S-Cl distance, r, and the Cl-S-Cl angle, θ. In terms of these parameters the principal moments of inertia of SCl_2^{35} may be expressed as

$$I_a = \frac{2mMr^2}{(2m + M)} \cos^2 \frac{\theta}{2} \tag{32}$$

$$I_b = 2mr^2 \sin^2 \frac{\theta}{2}$$

$$I_c = I_a + I_b$$

Table 5. Results of Fitting Rotational Constants to Seven Low J Transitions of $S^{32}Cl_2^{35}$ Approximately Corrected for Centrifugal Distortion†

Transition $J_\tau \rightarrow J'_{\tau'}$	Corrected‡ Frequency ν_o^* Mc	Centrifugal Distortion Correction $\Delta \nu_o$ Mc	Calculated Frequency ν_o^c Mc	$\nu_o^* - \nu_o^c$ Mc
$0_o \rightarrow 1_o$	17044.219	0.049	17044.098	0.121
$2_{-2} \rightarrow 2_o$	12687.947	-0.013	12687.893	0.054
$2_{-2} \rightarrow 3_{-2}$	26527.951	0.101	26527.770	0.181
$3_{-2} \rightarrow 4_{-4}$	10723.258	0.878	10723.576	-0.318
$4_{-2} \rightarrow 3_o$	11995.493	-0.327	11995.624	-0.131
$4_{-2} \rightarrow 4_o$	33615.872	-0.088	33615.970	-0.098
$4_{-4} \rightarrow 4_{-2}$	14573.251	-0.009	14573.217	0.034

† A = 14613.36 Mc, B = 2920.93 Mc, C = 2430.74 Mc

‡ T_1 = - 0.229 Mc, T_2 = 0.022 Mc, T_3 = - 0.011 Mc, T_4 = - 0.002 Mc, T_5 = 0.005 Mc, T_6 = - 0.00066 Mc

where M is the mass of the sulfur atom, m is the mass of the chlorine atom, and the information given by the previously mentioned electron diffraction work has been used to identify the C_2 axis of the molecule as the axis of intermediate moment of inertia*.

It is seen from Equations (32), then, that any two moments of inertia yield the two parameters r and θ. However, moments of inertia are not measured directly by microwave investigations of rotational spectra. Rather, as has been seen, it is the reciprocals of the moments of inertia which are measured. Since a molecule is not, in reality, a rigid body but is a rotating-vibrating assembly, the rotational constants appearing in a rigid rotor Hamiltonian should more properly be considered to be the instantaneous rotational constants averaged over the vibration. Moments of inertia derived from such rotational constants are customarily called effective moments of inertia, and a structure determined from them is called the effective structure.

For $S^{32}Cl_2^{35}$ the effective structure was calculated from the moments of inertia of Table 4 in the following manner. All possible combinations of moments of inertia taken two at a time were used to calculate a structure. The resulting structures were very nearly identical. They were averaged to obtain the structural parameters adopted as representing the effective structure of the molecule. This structure is given in Table 6.

The structure obtained in the microwave work is seen to compare well with the electron diffraction results. This comparison serves to further confirm the assignment of the b-axis.

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*This identification is substantiated by the microwave spectrum.

Table 6. Structure of $S^{32}Cl_2^{35}$*

	r (A)	θ
Microwave	2.014 ± 0.004**	102.8° ± 0.2°
Electron Diffraction	2.00 ± 0.02	103.0° ± 2.0°

*M_S = 31.982236 amu., $M_{Cl^{35}}$ = 34.97993.

**The errors indicated were chosen to span the range of r and θ obtained using the rotational constants of Tables 4 and 5.

Hyperfine Splittings and Quadrupole Coupling Constants

In order to determine the quadrupole coupling constants for the chlorine nuclei in sulfur dichloride, the hyperfine splittings of a majority of the spectral lines measured have been studied. The quadrupole coupling constants have been determined by measuring these splittings and utilizing these results to calculate the coupling constants in the following fashion.

As has been indicated in Chapter III, the first order energy level shifts resulting from the quadrupole interaction for the state $|\, J\, \tau)$ may be expressed as

$$\Delta E(J\tau\epsilon F) = \chi^{+}(J, \tau)\, \lambda_{\epsilon JF} \tag{33}$$

The frequency shifts for a transition $J_{\tau} \rightarrow J'_{\tau'}$ can then be expressed as

$$\Delta \nu(J\tau\epsilon F;\ J'\tau'\epsilon'F') = \Delta E(J'\tau'\epsilon'F') - \Delta E(J\tau\epsilon F) \tag{34}$$

$$= \chi^{+}(J'\tau')\, \lambda_{\epsilon' J' F'} - \chi^{+}(J\tau)\, \lambda_{\epsilon JF}$$

It will be remembered that the quantities $\lambda_{\epsilon JF}$ are tabulated and that the coupling, $\chi^{+}(J\tau)$, is a function of the rotational state of the system and of the quantities χ_{+} and χ_{-} which depend upon the quadrupole moment of the chlorine nucleus and the geometry of the molecule. Also recall that the quantity $\chi^{+}(J\tau)$ is a linear function of χ_{+} and χ_{-}.

The quantities χ_{+} and χ_{-} are the ones which are to be determined

from the hyperfine splittings of the rotational spectral lines. The discussion above shows that they will be obtained from experimentally observed hyperfine splittings by solution of a system of linear equations in two unknowns. Two independent hyperfine splittings are then all that are necessary to determine these two quantities. However, it is desirable to use more than two such splittings so as to have a slightly over-determined system.

This process has been described by Clayton (71) in connection with the determination of quadrupole coupling constants in a molecule containing a single quadrupolar nucleus. The mathematical problem is, however, identical to the one above. In this case the solution of the over-determined linear system was carried out in the fashion described in Appendix A in connection with the problem of determining rotational constants from the observed spectrum.

In this investigation a total of 71 hyperfine lines were measured in $S^{32}Cl_2{}^{35}$. Nineteen of the low J hyperfine lines which were members of symmetric patterns were chosen to be used to calculate χ_+ and χ_- as described above. It was felt that the fit obtained justified the use of only these lines in the fitting. In all cases poorly fitted lines are cases of weak transitions or lines which were close to Stark components. It is estimated that errors resulting from this interference with nearby Stark components are perhaps the largest encountered in the measurement of hyperfine splittings. In the worst cases these could be as large as 0.50 Mc. This much error is more than enough to account for the few large deviations found in these measurements. The results of this fitting are given in Table 7. All hyperfine lines measured are pre-

Table 7. Quadrupole Splittings in the Rotational Spectrum of $S^{32}Cl_2{}^{35}$ Which Were Used to Determine X_+ and X_-^*

Transition				Quadrupole Splitting		
J_τ	$J'_{\tau'}$	ϵF	$\epsilon' F'$	Measured $\Delta\nu^m$	Calculated $\Delta\nu^c$	$\Delta\nu^m - \Delta\nu^c$
				Mc	Mc	Mc
0_o	1_o	00	01	- 2.88	- 2.82	-0.06
		22	21	2.92	2.82	0.10
2_{-2}	2_o	22	22	-12.96	-13.06	0.10
		21	22	- 2.38	- 2.39	0.01
		02	22	8.58	8.29	0.29
		02	21	10.80	10.68	0.12
		02	02	13.18	13.06	0.12
2_{-2}	3_{-2}	02	03	- 4.33	- 4.24	-0.09
		22	23	4.22	4.24	-0.02
3_{-2}	4_{-4}	23	24	- 3.67	- 3.74	0.07
		03	04	3.63	3.74	-0.11
4_{-2}	3_o	24	23	- 1.37	- 1.42	0.05
		04	03	1.39	1.42	-0.03
4_{-4}	4_{-2}	24	25	-11.01	-11.18	0.17
		24	24	- 9.60	- 9.76	0.16
		23	04	- 1.28	- 1.42	0.14
		23	24	1.30	1.42	-0.12
		04	04	9.82	9.76	0.06
		04	23	11.14	11.18	-0.04

*The average deviation between measured and calculated splittings is 0.048 Mc and the standard deviation is .12 Mc. This fitting yields the values 8.932 Mc and -86.547 Mc for X_+ and X_- respectively.

sented in Appendix B, where they are compared to those calculated on the basis of the constants χ_+ and χ_- determined here.

The quantities χ_+ and χ_- and the equation

$$\chi_{aa} + \chi_{bb} + \chi_{cc} = 0$$

may be used to calculate the diagonal elements of the quadrupole coupling tensor expressed in the principal inertial axis system of the molecule. These are

$$\begin{aligned} \chi_{aa} &= -38.81 \text{ Mc} \\ \chi_{bb} &= -\ 8.93 \\ \chi_{cc} &= \ \ 47.74 \end{aligned} \tag{35}$$

This tensor is often given relative to a coordinate system in which the z-axis corresponds to the axis of the bond in which the quadrupolar nucleus is involved, in this case the S - Cl axis. The x-axis is perpendicular to the z-axis and lies in the plane of the molecule. The y-axis coincides with the c-axis. If one assumes that this x, y, z coordinate system is the principal axis system of the quadrupole coupling tensor, he can calculate the eigenvalues of the tensor using the diagonal elements given above if he knows the structure of the molecule. Using the structure found in an earlier section of this chapter, these eigenvalues are found to be

$$\begin{aligned} \chi_{zz} &= -91.81 \text{ Mc} \\ \chi_{xx} &= \ \ 44.07 \\ \chi_{yy} &= \ \ 47.74 \end{aligned} \tag{36}$$

Stark Effect of the $0_o \rightarrow 1_o$ Rotational Transition and Electric Dipole Moment

It was shown in Chapter III that so long as matrix elements of the quadrupole Hamiltonian off-diagonal in J and τ can be neglected, the Stark effect of the center component of the $0_o \rightarrow 1_o$ transition in a molecule of the symmetry type C_{2v} containing two identical nuclei of spin 3/2 can be treated as though the quadrupole interaction were absent. The shift of the frequency of this transition from the rigid rotor frequency is given by Equations (31) and (24). For the transition $0_o \rightarrow 1_o$, $\Delta M_J = 0$ the frequency shift is

$$\Delta \nu_S = \frac{2(\mu_b E)^2}{15}\left[\frac{-5 \times \lambda_b(00;\ 10)}{W^o(1,0) - W^o(0,0)} + \frac{\lambda_b(1,0;\ 2,\ -2)}{W^o(1,0) - W^o(2,\ -2)} + \frac{\lambda_b(1,0;\ 2,\ 2)}{W^o(1,0) - W^o(2,\ 2)}\right] \qquad (37)$$

where μ_b is the magnitude of the dipole moment of the molecule, E is the magnitude of the electric field, $\lambda_b(J, \tau;\ J', \tau')$ is the line strength of the rotational transition $J_\tau \rightarrow J'_{\tau'}$, and $W^o(J, \tau)$ is the unperturbed rigid rotor energy of the state J_τ.

The Stark splitting of the center component of the $0_o \rightarrow 1_o$ transition in $S^{32}Cl_2{}^{35}$ was measured at several electric fields, and the results of these measurements are given in Table 8. The dipole moment of the molecule was determined to be 0.36 Debye by a statistical fitting of the split-

Table 8. Stark Effect of the Center Component of the $O_o \rightarrow 1_o$ Transition in SCl_2^{35}

Stark Voltage	Calculated Stark Splitting	Measured Stark Splitting
(Volts)	(Mc)	(Mc)
168	.45	.63
244	.95	1.05
410	2.68	2.68
510	4.14	4.20
550	4.82	4.88

tings at 410, 510, and 550 volts using Equation (37). The data at 168 and 244 volts were not used because it was felt that the Stark components were not completely separated from the absorption line. The fact that at 168 and 244 volts the measured splittings are appreciably greater than those calculated on the basis of the above dipole moment serves to corroborate this decision.

The rigid rotor energies used in this calculation were obtained from the rotational constants given on page 36 in Table 4. The line strengths were evaluated using closed form expressions given by Gora (72). Other constants used are

$$d = 0.4662 \text{ cm}$$

$$\mu E = 0.50348 \text{ Mc/Debye volt/cm}$$

where d is the distance between the center electrode of the absorption cell and the walls of the cell parallel to it.

This determination of the dipole moment of SCl_2 is not as accurate as an analysis of the Stark effect usually yields. The splitting is small because the dipole moment is small and the denominators in Equation 37 are large. Very large values of E cannot be used because the inhomogeneity of the electric field broadens the Stark lines. Therefore, the dipole moment is given to only two significant digits. There appears to be no previous determination of the dipole moment.

CHAPTER V

CONCLUSIONS

The study of the microwave spectrum of sulfur dichloride reported upon in this thesis has confirmed that the molecule has the structural form given by the early electron diffraction studies. The S - Cl distance was found to be 2.014 ± 0.004 A and the Cl - S - Cl angle was found to be 102.8° ± 0.2°. These values were calculated from measured effective rotational constants which are A = 14613.3 Mc, B = 2920.86 Mc, and C = 2430.69 Mc and which yield - 0.919530 for Ray's asymmetry parameter, κ. The values of the effective rotational constants given above yield a best fit in the least squares sense to the low J spectrum of the molecule. However, they do not predict the frequencies of all observed rotational transitions within the experimental error. The small discrepancies are attributed to centrifugal distortion effects which have not been included in the treatment rather than to a misassignment of transitions. Supporting this conclusion is the fact that the electric quadrupole coupling has been studied for the majority of the lines reported and has been found to be in agreement with predictions of first-order quadrupole theory. Attempts to include centrifugal distortion effects in the treatment have failed because a sufficient number of high J transitions could not be measured.

The existing quadrupole coupling theory for two identical nuclei has been proven adequate for describing the quadrupole interactions in

$S^{32}Cl_2{}^{35}$, and a least squares fitting of the hyperfine components of the $0_0 \rightarrow 1_0$, $2_{-2} \rightarrow 2_0$, $2_{-2} \rightarrow 3_{-2}$, $3_{-2} \rightarrow 4_{-4}$, $4_{-2} \rightarrow 3_0$, and $4_{-4} \rightarrow 4_{-2}$ transitions yields quadrupole coupling constants χ_{aa} = - 38.81 Mc, χ_{bb} = - 8.93 Mc and χ_{cc} = 47.74 Mc. The hyperfine components of other lines as calculated using these constants prove to be an acceptable fit to those which were measured. These constants and the structure yield - 91.81 Mc for χ_{zz}, the value of the component of the quadrupole coupling tensor along the S - Cl bond axis.

Although no microwave studies have been reported for other molecules in which a sulfur atom is bonded to two chlorine atoms, it is possible to compare some of the above parameters with those for other molecules. The S - Cl distance in $S^{32}Cl_2{}^{35}$ compares favorably with those in S_2Cl_2, $SOCl_2$, and SO_2Cl_2 which are 1.99 ± 0.03 A, 2.07 ± 0.03 A, and 1.99 ± 0.02 A and which were obtained by K. J. Palmer using electron diffraction techniques (73). An investigation of the microwave spectrum of OCl_2 (74, 75) has yielded the value - 143 Mc for χ_{zz}. Since χ_{zz} is - 109.6 Mc in atomic Cl and it increases to zero when one p electron is added and decreases to approximately 2 × (- 109.6) Mc when one p electron is removed, these results indicate that the Cl atoms in SCl_2 have some of the character of Cl^- while those in OCl_2 have some of the character of Cl^+.

An analysis of Stark effect of the center component of the $0_0 \rightarrow 1_0$ triplet has yielded a value of 0.36 ± 0.01 Debye for the electric dipole moment of $S^{32}Cl_2{}^{35}$.

It has not proven possible to measure the spectra of the isotopic species of sulfur dichloride containing Cl^{37} because of the low intensity of their spectra. This low intensity is attributed to the smaller number

of molecules per unit volume in the case of SCl_2^{37} and to the fact that all the rotational levels of $SCl_2^{35,37}$ are split into 16 components by the quadrupole interaction with the result being a decrease in the intensity of individual transitions in this molecule.

In the course of performing the calculations necessary for interpretation of the results of this work, it proved desirable to extend tables of certain numbers useful for a study of quadrupole interactions in asymmetric rotors. These are the tables of $\lambda_{\epsilon JF}$ and $A(J, \tau)$, $B(J, \tau)$ presented in Appendix C and D respectively.

The results of this investigation have been sent to Dr. P. G. Favero who intends to study the high frequency spectrum of sulfur dichloride. It is hoped that his results may allow the inclusion of centrifugal distortion effects in the analysis of this spectrum.

APPENDICES

APPENDIX A

PROGRAMS FOR THE DIGITAL COMPUTATION OF TRANSITION FREQUENCIES AND ANALYSIS OF ROTATIONAL SPECTRA OF RIGID ASYMMETRIC TOP MOLECULES

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PROGRAMS FOR THE DIGITAL COMPUTATION OF TRANSITION FREQUENCIES AND ANALYSIS OF ROTATIONAL SPECTRA OF RIGID ASYMMETRIC TOP MOLECULES

The study and analysis of the rotational spectrum of a molecule can be divided into three basic parts. The study begins with rough measurement of the spectrum and assignment of quantum numbers specifying the initial and final rotational energy states involved in the observed transitions. The assignment of quantum numbers is followed by precise measurement of all observable transitions which are of interest, and this measurement is in turn followed by a numerical analysis of the observed spectrum which yields the molecular moments of inertia*

Invariably an approximate spectrum calculated from an assumed molecular structure has proven to be of extreme value in identifying the observed spectral lines of asymmetric rotor molecules. When sufficient transitions have been measured to yield the moments of inertia of the molecule, these can be used to calculate a much more accurate spectrum. Such a spectrum greatly facilitates the locating of weak lines in the spectrum. These facts prompted the developement of the programs presented below. One of them calculates the spectrum of a rigid asymmetric top molecule from given principal moments of inertia while the other

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* The "rigid rotor" approximation is being considered here.

calculates moments of inertia from measured spectral frequencies.

Calculation of Rotational Spectrum from Moments of Inertia

Definition and Solution of the Problem

It was shown in Chapter III that the problem of obtaining the rotational spectrum of a rigid asymmetric rotor reduces to the diagonalization of certain matrices to obtain the energy eigenvalues and subsequent application of the selection rules to obtain the transition frequencies.

The matrices diagonalized in this program are not identical to those described in Chapter III. For computational ease, use has been made of an observation due to Gora (76). He noted that all four submatrices have the common element $F \times J \times (J + 1)$ appearing as a summand on the diagonal. Hence this term may be subtracted from the diagonal elements and added to the eigenvalues of the resultant matrix.
The energy is then

$$E_\tau^J = \frac{1}{2}(A + C) \times J \times (J + 1) + \frac{1}{2}(A - C)\left[F \times J \times (J + 1) + E_\tau^{J*}(\kappa)\right] \quad (38)$$

where the numbers $E_\tau^{J*}(\kappa)$ are the eigenvalues of the $E^{\pm}$; $O^{\pm}$ matrices of Chapter III without the term $F \times J \times (J + 1)$ on the diagonal.

Computationally the process consists of four steps: the evaluation of the matrix elements of the reduced Hamiltonian, the evaluation of the eigenvalues of these matrix elements, the evaluation of the energies from these eigenvalues, and application of the selection rules to obtain the transition frequencies.

Numerically the matrix elements and energies are simply evaluated,

as they are simple algebraic expressions.

The eigenvalues of the reduced energy matrices can be found very accurately since these matrices are of tri-diagonal form. That is, they are real symmetric matrices with only the diagonal and first off-diagonal elements non zero.

In the algorithm described below the eigenvalues are found by a method due to Givens (77). The procedure is a modification of an ALGOL 60 routine devised by J. H. Wilkinson (78). The method is based upon the following theorem (79).

Given a symmetric tri-diagonal N × N matrix, M, with diagonal elements $C_1, C_2, \ldots, C_n$ and off-diagonal elements $b_1, b_2, \ldots, b_{n-1}$ with $b_i \neq 0$ for any i, then for any number λ, define the sequence $f_0(\lambda), f_1(\lambda), \ldots, f_N(\lambda)$ by the relations*

$$
\begin{aligned}
f_0(\lambda) &= 1 \\
f_1(\lambda) &= (C_1 - \lambda) \\
&\vdots \\
f_i(\lambda) &= (C_i - \lambda)\, f_{i-1}(\lambda) - b^2_{i-1}\, f_{i-2}(\lambda)
\end{aligned}
\tag{39}
$$

Associate a sign with each of the $f_i(\lambda)$ as follows. If $f_i(\lambda) \neq 0$ then this sign is the true sign of $f_i(\lambda)$. If $f_i(\lambda) = 0$, then its sign is taken to be the opposite of that of $f_{i-1}(\lambda)$.

Then the number, $A(\lambda)$, of agreements in sign between consecutive members of the sequence is equal to the number of eigenvalues strictly

---

*This sequence is the sequence of principal minors of the determinant of the matrix M - λI.

greater than λ.

This theorem may be used to locate all eigenvalues of such a matrix very accurately in the following fashion.

First calculate the infinity norm of the matrix,

$$\text{norm} = \max_{i} \sum_{j} | A_{ij} | \tag{40}$$

That is, calculate the N numbers obtained by summing absolute values of all elements in a given row; then take the maximum of these N numbers. If λ_i is any eigenvalue of the matrix $M = (A_{ij})$, it is then true that

$$| \lambda_i | \leq \text{norm}. \tag{41}$$

Let the eigenvalues be ordered such that

$$\lambda_1 > \lambda_2 \cdots > \lambda_N$$

To find λ_1:

Let g_o = norm, h_o = - norm

then $g_o \geq \lambda_1 \geq h_o$. Compute $A[(g_o + h_o)/2]$.

If $A[(g_o + h_o/2] \geq 1$ take $h_1 = (g_o + h_o)/2$; $g_1 = g_o$.

If $A[(g_o + h_o/2] < 1$ take $g_1 = (g_o + h_o)/2$; $h_1 = h_o$.

Then $(g_1 - h_1) = (g_o - h_o)/2$ and

$A[h_1] \geq 1$, $A[g_1] < 1$.

After i such steps λ_1, is located in the interval (h_i, g_i) of width $(g_o - h_o)/2^i$. λ_2 is then found in identically the same fashion except in the first step let $g_o = \lambda_1$. Similarly for λ_r let $g_o = \lambda_{r-1}$, $r > 1$. The process may be terminated after a fixed number of steps or when $(g_o - h_o)/2^i$ is small enough to give the eigenvalue to the desired accuracy. This bisection process is employed in the program given below.

The asymmetric rotor selection rules are handled in the following manner.

An integer is associated with each of the four symmetry types ee, eo, oo, oe as follows: ee = 1, eo = 2, oo = 3, oe = 4. Then for a given value of J, say J', the integers associated with the levels J'_τ, $\tau = J', J' - 1, \cdots, -J'$, and $(J' + 1)_\tau$, $\tau = J' + 1, J', \cdots, -J' - 1$ are calculated. For each energy level J_τ all levels $J_{\tau+1}$, $J_{\tau+2}$, $\cdots$, J_J, $(J + 1)_{-J-1}$, $(J + 1)_{-J}$, $\cdots$, $(J + 1)_{J+1}$ are inspected and if they have the proper symmetry required by the selection rules, the energies are subtracted and the difference is printed as a frequency.

The input to the computer is the name of the molecule, a lower limit on the quantum number J, (the program computes energies for J between a specified lower limit, usually 0, and a specified upper limit), an upper limit on J, instructions specifying which transitions to calculate, rotational constants $A \geq B \geq C$, a lower limit on desired frequencies and an upper limit on desired frequencies. This information is given on two cards which must have the form indicated in Table 9.

The output is fully formated and is, therefore, self-explanatory.

A listing of the cards complete with sample data cards and the output of a sample problem is given on the following pages. The sample prob-

Table 9. Data Card Format for Program to Calculate Rotational Spectrum

Card #	Columns	Contents	Sample	Remarks
1	1 - 24	Name of Molecule	S 0(16)0(18)	Any 24 characters
	25 - 80	Blank		Not read by machine
2	1 - 3	Lower limit on J	0	Three digit integer, right justified, leading zeros may be dropped
	4 - 6	Upper limit on J	25	As above
	7 - 8	μ_a transitions	0	Right justified, 0 = do not calculate, 1 = do calculate
	9 - 10	μ_b transitions	1	As above
	11 - 12	μ_c transitions	0	As above
	13	Blank		
	14 - 28	A	3062.5	Decimal point in column 20
	29 - 43	B	2969.9	" " " " 35
	44 - 58	C	1969.8	" " " " 50
	59 - 68	Lower limit on frequency	6000.0	" " " " 65
	69 - 78	Upper limit on frequency	10000.0	" " " " 75
	79 - 80	Blank		

lem worked was the calculation of the spectrum of oxygen difluoride through $J = 5$ for the rotational constants given by Pierce, DiCianni and Jackson (80).

Listing of Program Cards

```
                    COMPILATION CARD GOES HERE
?30         END-OF-FILE CARD                                              ?
 LABEL  0000000000XXXXXX0010000001
$ CARD LIST
          BEGIN
COMMENT   THIS PROGRAM COMPUTES THE ROTATIONAL ENERGIES AND TRANSITIONS
          FOR AN ASYMMETRIC TOP TYPE MOLECULE GIVEN THE ROTATIONAL
          CONSTANTS IN MEGACYCLES PER SEC. ;
INTEGER ARRAY MU[0:2] ;
ALPHA ARRAY   NAME [0:3] ;
INTEGER       J,N,JL,JU ;
REAL          A,B,C,KAPPA,     H,NUL,NUU,F1,G1 ;
LABEL         WORK,EXIT ;
FILE IN       CARD (2,10) ;
FORMAT IN     FMI1 (4A6/2I3,3I2,X1,3F15.8,2F10.3) ;
LIST          INP ( FOR N := 0 STEP 1 UNTIL 3 DO NAME[N],JL,JU,MU[0],
                        MU[1],MU[2],A,B,C,NUL,NUU) ;
WORK:         READ (CARD,FMI1,INP) [EXIT] ;
              CLOSE (CARD,RELEASE) ;
                   BEGIN
REAL ARRAY    DIAG,SUBD,DUM[0:(JU+2) DIV 2],W[JL:JU,-JU:JU],FF[0:JU+1] ;
INTEGER       R,S,K ;
INTEGER ARRAY SS[0:1,-JU-1:JU+1],F[0:3],SEL[0:2,0:3] ;
LABEL         EP,EM,OP,OM,EXIT1,R1,R2,R3,R4,TBS ;
SWITCH        MATRIX := R1,R2,R3,R4 ;
FORMAT OUT    FMO1 (X20,4A6//X9,"A",X16,"B",X16,"C",X10,"KAPPA"/
                   3F16.4,F14.7/),
              FMO2 (2I5,X6,F12.4),
              FMO3 (2(X3,2I5),F17.4),
              TITLE(X4,"J",X3,"TAU",X6,"ENERGY  MCS."),
         TITLE3 ("MU A FREQUENCIES,",F10.1,"  TO  ",F10.1,X3,"MCS.",//),
         TITLE4 ("MU B FREQUENCIES,",F10.1,"  TO  ",F10.1,X3,"MCS.",//),
         TITLE5 ("MU C FREQUENCIES,",F10.1,"  TO  ",F10.1,X3,"MCS.",//),
              TITLE6 (X5,"LOWER STATE  UPPER STATE   FREQUENCY, MCS."/
                      X7,"J   TAU      J   TAU") ;
```

```
LIST          OUT1 (FOR J := 0 STEP 1 UNTIL 3 DO NAME[J],A,B,C,KAPPA),
              OUT2 (FOR J := JL STEP 1 UNTIL JU DO
                   FOR K := -J STEP 1 UNTIL J DO [J,K,W[J,K]])};
FILE OUT      HSP 1(1,15) };
              KAPPA := (2×B-A-C) / (A-C) };
              F1 := (KAPPA - 1) / 2 };
              H ← - (KAPPA +1) / 2 };
              G1 := - (KAPPA - 3) / 2 };
              FOR J := JL STEP 1 UNTIL JU DO
        BEGIN  R := 0 };
              FOR N := 0 STEP 1 UNTIL J-1 DO
              FF[N] := (J-N)×(J-N+1)×(J+N)×(J+N+1)/4 };
              FF[J] := FF[J+1] := 0 };
EP: BEGIN
              S      ← ENTIER(((2×J+3) + (-1)*J)/4) };
                   BEGIN
              FOR N ← 1 STEP 1 UNTIL S      DO
                        BEGIN
              DIAG[N] ← F1× J × (J + 1) + G1× ((2×(N-1))*2) };
              SUBD[N] ← H × SQRT (FF[  2×N-1])
                        END };
              SUBD[1] ← (SQRT(2)) × SUBD[1] };
              SUBD[S] := 0 };
              GO TO TBS };
R1:           FOR N ← 1 STEP 1 UNTIL S DO
              W[J,J-1+(-1)*J-4×(N-1)] ← ((A+C)×J×(J+1)+(A-C)×DUM[N])/2
                   END
              END };
EM:           BEGIN
              S     := ENTIER ((2×J-1+(-1)*J)/4) };
              IF S = 0 THEN BEGIN R := R+1 } GO TO OP END ELSE
                   BEGIN
              FOR N ← 1 STEP 1 UNTIL S DO
                        BEGIN
              DIAG[N] ← ((2×N)*2) × G1+ F1× J × (J + 1) };
```

```
                SUBD[N] ←H × SQRT (FF[  2×N + 1])
                          END ;
                SUBD[ S] := 0 ;
                GO TO TBS ;
R2:             FOR N ← 1 STEP 1 UNTIL S DO
                W[J,J-2+(-1)*J-4×(N-1)] ← ((A+C)×J×(J+1)+(A-C)×DUM[N])/2
                     END
                END ;
OP:             BEGIN
                S    := ENTIER ((2×J+1-(-1)*J)/4) ;
                IF S = 0 THEN
                GO TO OM
                ELSE
                     BEGIN
                FOR N ← 1 STEP 1 UNTIL S DO
                          BEGIN
                DIAG[N] ← ((2×N-1)*2)×G1+F1× J × (J + 1 ) ;
                SUBD[N] ← H × SQRT (FF[  2×N])
                          END ;
                DIAG[1] ← DIAG[1] + H × SQRT (FF[  0]) ;
                SUBD[S] := 0 ;
                GO TO TBS ;
R3:             FOR N ← 1 STEP 1 UNTIL S DO
                W[J,J-2-(-1)*J-4×(N-1)] ← ((A+C)×J×(J+1)+(A-C)×DUM[N])/2
                     END
                END ;
OM:             BEGIN
                S    := ENTIER ((2×J+1-(-1)*J)/4) ;
                IF S = 0 THEN
                GO TO EXIT1
                ELSE
                     BEGIN
                FOR N ← 1 STEP 1 UNTIL S DO
                          BEGIN
                DIAG[N] ← ((2×N-1)*2) × G1+ F1× J × (J + 1) ;
```

```
                SUBD[N] ← H × SQRT (FF[  2×N])
                          END ;
                DIAG[1] ← DIAG[1] - H × SQRT (FF[  0]) ;
                SUBD[S] := 0 ;
                GO TO TBS ;
R4:             FOR N ← 1 STEP 1 UNTIL S DO
                W[J,J-1-(-1)*J-4×(N-1)] ← ((A+C)×J×(J+1)+(A-C)×DUM[N])/2 ;
                GO TO EXIT1
                     END
                END ;
TBS:       BEGIN
INTEGER         J,A1 ;
REAL            L,G,H,LAMBDA,P1,Q1,Y ;
REAL            NORM ;
ARRAY           P[1:S] ;
LABEL           ONE,TWO ;
                BEGIN
                R := R + 1 ;
                IF S = 1 THEN
                     BEGIN
                DUM[1] := DIAG[1] ;
                GO TO TWO ;
                     END ;
ONE:            NORM := ABS(DIAG[1] ) + ABS(SUBD[1]) ;
                FOR N ← 2 STEP 1 UNTIL S DO
                     BEGIN
                L := ABS(SUBD[N-1]) + ABS(DIAG[N]) + ABS(SUBD[N]) ;
                IF L > NORM THEN NORM ← L
                     END ;
                FOR N ← 1 STEP 1 UNTIL S-1 DO
                     BEGIN
                IF SUBD[N] = 0 THEN P[N+1] := (NORM*2) × 1.0@-43
                ELSE P[N+1] := SUBD[N] * 2
                     END ;
                P[1] ← 0 ;
```

```
                DUM[0] := NORM ;
                FOR K ← 1 STEP 1 UNTIL S DO
                     BEGIN
                G ← DUM[K-1] ;
                H ← -NORM ;
                FOR J := 1 STEP 1 WHILE (ABS(G-H) ≥ 1.0@-08) DO
                          BEGIN
                LAMBDA ← (G + H) / 2 ;
                               BEGIN
                P1 ← 0 ;
                Q1 ← 1 ;
                A1 ← 0 ;
                FOR N ← 1 STEP 1 UNTIL S DO
                                    BEGIN
                Y ← (DIAG[N] - LAMBDA) × Q1 - P[N] × P1 ;
                P1 ← Q1 ;
                Q1 ← Y ;
                IF P1 ≥ 0 EQV Q1 ≥ 0 THEN A1 ← A1 + 1
                                     END ;
                IF Q1 = 0 AND P1 > 0 THEN A1 ← A1 - 1
                                    END ;
                IF A1 ≥ K THEN H ← LAMBDA ELSE G ← LAMBDA
                                    END ;
                DUM[K] := (G + H) / 2
                     END ;
TWO:            GO TO MATRIX[R]
                END
          END ;
EXIT1:    END ;
                WRITE (HSP[PAGE]) ;
                WRITE(HSP,FMO1,OUT1) ;
                WRITE (HSP,TITLE) ;
                WRITE(HSP,FMO2,OUT2) ;
                WRITE (HSP[PAGE]) ;
                FOR N ← 0,3 DO F[N] ← 3 ;
```

```
FOR N ← 1,2 DO F[N] ← 7 ;
FOR N ← 0 STEP 1 UNTIL 2 DO SEL[N,0] ← 1 ;
FOR N ← 0 STEP 1 UNTIL 2 DO SEL[N,1] ← N + 2 ;
SEL[1,2] ← SEL[2,2] ← SEL[0,1] ;
SEL[0,2] ← SEL[2,3] ← SEL[1,1] ;
SEL[0,3] ← SEL[1,3] ← SEL[2,1] ;
FOR N ← 0 STEP 1 UNTIL 2 DO
IF MU[N] ≠ 0 THEN
     BEGIN
WRITE (HSP[PAGE]) ;
WRITE(HSP,FMD1,OUT1) ;
IF N = 0 THEN WRITE (HSP,TITLE3,NUL,NUU) ELSE
IF N = 1 THEN WRITE (HSP,TITLE4,NUL,NUU) ELSE
IF N = 2 THEN WRITE (HSP,TITLE5,NUL,NUU) ;
WRITE (HSP,TITLE6) ;
FOR S := JL STEP 1 UNTIL JU DO
          BEGIN
FOR J ← 0 STEP 1 UNTIL 3 DO
                BEGIN
FOR  K ← -S+J STEP 4 UNTIL S DO
SS[0,K] ← ((-1)*(J+S+1) + F[J]) DIV 2 ;
FOR K ← -S-1+J STEP 4 UNTIL S+1 DO
SS[1,K] ← ((-1)*(J+S+2) + F[J]) DIV 2
                END ;
FOR R ← -S STEP 1 UNTIL S DO
                BEGIN
J := S ;
FOR K ← R+1 STEP 1 UNTIL J DO
IF (((SS[0,R] = SEL[N,0]) AND (SS[0,K] = SEL[N,1]))
OR  ((SS[0,R] = SEL[N,1]) AND (SS[0,K] = SEL[N,0]))
OR  ((SS[0,R] = SEL[N,2]) AND (SS[0,K] = SEL[N,3]))
OR  ((SS[0,R] = SEL[N,3]) AND (SS[0,K] = SEL[N,2]))) THEN
                     BEGIN
DIAG[1] ← W[J,K] - W[S,R] ;
IF ((ABS(DIAG[1]) ≤ NUU) AND (ABS(DIAG[1]) ≥ NUL)) THEN
```

```
                WRITE (HSP[DBL],FMD3,S,R,J,K,DIAG[1]) ;
                                    END ;
                IF S ≠ JU THEN      BEGIN
                J := S+1 ;
                FOR K ← -J STEP 1 UNTIL J DO
                IF (((SS[0,R] = SEL[N,0]) AND (SS[1,K] = SEL[N,1]))
                OR  ((SS[0,R] = SEL[N,1]) AND (SS[1,K] = SEL[N,0]))
                OR  ((SS[0,R] = SEL[N,2]) AND (SS[1,K] = SEL[N,3]))
                OR  ((SS[0,R] = SEL[N,3]) AND (SS[1,K] = SEL[N,2]))) THEN
                                    BEGIN
                DIAG[1] ← W[J,K] - W[S,R] ;
                IF ((ABS(DIAG[1]) ≤ NUU) AND (ABS(DIAG[1]) ≥ NUL)) THEN
                WRITE (HSP[DBL],FMD3,S,R,J,K,DIAG[1]) ;
                                    END
                                    END
                                  END
                               END
                          END ;
                          END ;
EXIT:           END .
?30         END-OF-FILE CARD                                              ?
 LABEL   000000000CARD    0010000001


                        SAMPLE DATA CARDS


OXYGEN DIFLUORIDE
  0   5 0 1 0   58782.63        10896.431        9167.412       13800.0    60000.0


                      END OF SAMPLE DATA CARDS

?31         END-OF-DECK-CARD                                              ?
```

Output from Sample Problem

Oxygen Difluoride

A	B	C	KAPPA
58782.6300	10896.4310	9167.4120	- 0.9303029

J	TAU	MC
0	0	0.0000
1	-1	20063.8430
1	0	67950.0420
1	1	69679.0610
2	-2	60145.5482
2	-1	106348.7090
2	0	111535.7660
2	1	255194.3630
2	2	255240.3440
3	-3	120153.3699
3	-2	163918.3441
3	-1	174291.6934
3	0	315385.8920
3	1	315615.5801
3	2	559167.8000
3	3	559168.5647
4	-4	199950.8836
4	-3	240625.9683
4	-2	257910.8084
4	-1	395605.4949
4	0	396293.0307
4	1	639512.8817
4	2	639518.2317
4	3	980685.5352
4	4	980685.5458
5	-5	299360.1745
5	-4	336429.3475
5	-3	362343.2492
5	-2	495822.5363
5	-1	497419.9119
5	0	739982.2642
5	1	740003.6476
5	2	1081106.9237
5	3	1081107.0185
5	4	1519768.4783
5	5	1519768.4784

Oxygen Difluoride

A	B	C	KAPPA
58782.6300	10896.4310	9167.4120	- 0.9303029

MU B Frequencies 7,000 to 70,000 MC

LOWER STATE J	LOWER STATE TAU	UPPER STATE J	UPPER STATE TAU	FREQUENCY, MC
0	0	1	0	67950.0420
1	-1	1	1	49615.2180
1	0	2	-2	- 7804.4938
2	-2	2	0	51390.2178
2	-1	3	-3	13804.6609
3	-3	3	-1	54138.3235
3	-2	4	-4	36032.5396
3	0	4	-2	-57475.0836
4	-4	4	-2	57959.9248
4	-3	5	-5	58734.2062
4	-1	5	-3	-33262.2457
4	0	5	-4	-59863.6832
5	-5	5	-3	62983.0747

Calculation of Rotational Constants from Spectral Frequencies

Definition and Solution of the Problem

It was desired to develop a program that would give rotational constants which are an approximation to those which fit the observed spectrum in the least squares sense. Also, the program should converge from nearly any starting point. The second criterion proved to be the more difficult to satisfy. A previous program (81) apparently would not work unless the user had a very good initial guess as to the values of A, B, and C.

In order to create a program which would converge from a poor starting point, it proved necessary to utilize only transitions for which $J \leq 4$. This results from the fact that the numerical methods used in the minimization required the second derivatives of the energy eigenvalues, and numerical differentiation of these eigenvalues proved too slow to be useful.

Specifically the problem is as follows. For those levels of interest, $J \leq 4$, the reduced energy matrices are of order three or less; and, therefore, closed-form expressions may be given for the energies. These expressions for quadratic secular equations have been given by Gordy et al. (82), and the cubics are solved in this program. The measured frequencies can then be expressed as differences of these closed-form expressions. Since there are three unknowns, A, B, and C, at least three frequencies must be measured in order to determine the unknowns.* If the n measured frequencies are denoted by a_i, $i = 1, 2, \ldots, n$ and the calculated values are $f_i(A, B, C)$, $i = 1, 2, \ldots, n$; then the problem

*Three frequencies will not always determine the rotational constants, e.g. three Q-branch transitions give a very poor fit.

is to solve the system

$$f_i(A, B, C) - a_i = 0, \; i = 1, 2, \ldots, n \geq 3 \tag{42}$$

for A^o, B^o, C^o such that

$$\sum_{i=1}^{n} \left[f_i(A^o, B^o, C^o) - a_i \right]^2 \leq \sum_{i=1}^{n} \left[f_i(A, B, C) - a_i \right]^2 = S(A, B, C) \tag{43}$$

for any A, B, C. That is solve the system (42) in the least squares sense. The problem is non-trivial since the functions $f_i(A, B, C)$ are non-linear functions of A, B, and C.

The problem is handled in the following fashion. Let $\underline{A}^j = (A^j, B^j, C^j)$ be a j^{th} approximation to the solution $(A^o, B^o, C^o) = \underline{A}^o$ which is assumed to exist.

We require that the function S(A, B, C) have a relative minimum at $\underline{A}^o$. This means

$$\left. \frac{\partial S}{\partial A_k} \right|_{\underline{A} = \underline{A}^o} \equiv 0; \; k = 1, 2, 3 \tag{44}$$

where $A_1 = A$, $A_2 = B$, and $A_3 = C$.

Now

$$\left. \frac{\partial S}{\partial A_k} \right|_{\underline{A}^o} = 2 \sum_{l} \left[f_l(\underline{A}^o) - a_l \right] \left. \frac{\partial f_l}{\partial A_k} \right|_{\underline{A}^o}; \; k = 1, 2, 3 \tag{45}$$

This is a system of three non-linear equations in three unknowns; it is linearized as follows.

By Taylor's theorem (83)

$$\left.\frac{\partial f_l}{\partial A_k}\right|_{\underline{A}^o} \approx \left.\frac{\partial f_l}{\partial A_k}\right|_{\underline{A}^j} + \left.\frac{\partial^2 f_l}{\partial A_k \partial A_m}\right|_{\underline{A}^j} (A^o{}_m - A^j{}_m);\ k = 1, 2, 3 \qquad (46)$$

and

$$f_l(\underline{A}^o) \approx f_l(\underline{A}^j) + \left.\frac{\partial f_l}{\partial A_m}\right|_{\underline{A}^j} (A^o{}_m - A^j{}_m) \qquad (47)$$

where repeated indices are summed over. Substitution into Equation (45) and the dropping of non-linear terms gives

$$\sum_n \left\{ \sum_l \left[\left.\frac{\partial f_l}{\partial A_n}\right|_{\underline{A}^j} \left.\frac{\partial f_l}{\partial A_k}\right|_{\underline{A}^j} + (f_l(\underline{A}^j) - a_l) \left.\frac{\partial^2 f_l}{\partial A_k \partial A_n}\right|_{\underline{A}^j} \right] (A^o{}_n - A^j{}_n) =$$

$$\sum_l \left[a_l - f_l(\underline{A}^j) \right] \left.\frac{\partial f_l}{\partial A_k}\right|_{\underline{A}^j};\ k = 1, 2, 3 \qquad (48)$$

This is a system of three linear equations in three unknowns. The unknowns being the three components of the vector $\underline{\Delta A} = \underline{A}^o - \underline{A}^j$. Solution yields a better approximation to $\underline{A}^o$ through

$$\underline{A}^{j+1} = \underline{A}^j + \underline{\Delta A} \qquad (49)$$

In the present program this system is solved by a Gauss-Jordan technique (84). If the second derivatives in Equations (48) are set equal to zero Kneubühl's (85) method results. It does not always converge. Since the functions f_i are non-linear, several iterations are required to reach the minimum.

This method is often called the Newton-Rapheson method. The present program incorporates a modification due to Hartely (86) and Strand (87) which in many cases insures convergence. Essentially the modification is to alter the correction vector $\underline{\Delta A}$ by multiplying it by a scalar t which is such that $-1.75 \leq t \leq 1.25$ and to look for a minimum of $S(\underline{A})$ along the line $\underline{A}^j + t\,\underline{\Delta A}$.

The present program will iterate a specified number of times unless the function S fails to change from one iteration to the next at which point it stops. Results are printed after each iteration.

The information which the program accepts as input is the name of the molecule, the number of frequencies to be fitted, the number of iterations to be made, initial approximations to the rotational constants, and quantum numbers and frequencies for each transition to be fitted. This data must be presented as shown in Table 10; otherwise the computer will not run the program.

A listing of the cards complete with sample data cards and the output of a sample problem is given below. The sample problem is the fitting of the seven frequencies for $J \leq 4$ measured by Pierce, DiCianni and Jackson (88) for the molecule oxygen difluoride.

Table 10. Data Card Format for Program to Analyze Spectrum

Card Number	Columns	Contents	Sample	Remarks
1.	1-24	Name of molecule	SO2	Any 24 characters
	25-80	Blank		
2.	1-4	# Transitions	5	Right justified, leading zeroes may be dropped
	5-8	# Iterations	20	Right justified, leading zeroes may be dropped
	9-22	A	14613.2	Decimal point in Col. 17
	23-36	B	6039.1	Decimal point in Col. 31
	37-50	C	5069.9	Decimal point in Col. 45
	51-80	Blank		
3.	1-3	J of lower state	0	Right justified
	4	Blank		
	5-7	Tau of lower state	0	Right justified, - sign in column 5
	8-11	Blank		
	12-14	J of upper state	1	Right justified
	15	Blank		
	16-18	Tau of upper state	-01	Right justified, - sign in column 16
	19	Blank		
	20-35	Frequency	17044.22	Decimal point in column 27
4.	Same format as 3, one card per transition			

Listing of Program Cards

```
                    COMPILATION CARD GOES HERE
?30         END-OF-FILE CARD                                              ?
 LABEL  0000000000XXXXX0010000001
$ CARD LIST
          BEGIN
          COMMENT THIS PROGRAM COMPUTES THE ROTATIONAL CONSTANTS OF A
          RIGID ROTOR FROM GIVEN SPECTRAL FREQUENCIES ;
FILE OUT       FO1 1(1,15) ;
INTEGER        N,J,M1 ;
REAL ARRAY     A[0:2] ;
ALPHA ARRAY    NAME[0:3] ;
FILE IN        FI1 (1,10) ;
FORMAT IN      FMI1 (4A6) ,
               FMI2 (2I4,3F14.5) ;
LIST           INP1 (FOR J ← 0 STEP 1 UNTIL 3 DO NAME[J]),
               INP2 (N,M1,FOR J ← 0 STEP 1 UNTIL 2 DO A[J]) ;
               READ (FI1,FMI1,INP1) ;
               READ (FI1,FMI2,INP2) ;
               N ← N - 1 ;
               BEGIN
INTEGER        M ;
INTEGER ARRAY  JU,JL,TU,TL[0:N] ;
REAL ARRAY     NU[0:N] ;
FORMAT IN      FMI3 (2(I3,X1),X3,2(I3,X1),F16.8) ;
LIST           INP3 (FOR J ← 0 STEP 1 UNTIL N DO
                    [JL[J],TL[J],JU[J],TU[J],NU[J]]) ;
               READ (FI1,FMI3,INP3) ;
               CLOSE(FI1,RELEASE) ;
               M ← 0 ;
                    BEGIN
INTEGER        I,K,R ;
REAL           S,DS,SUM,TT ;
REAL ARRAY     X[0:2,0:3],NUC,D1,D2[0:N],DELT[0:N,0:2],DA[0:2],
                    T,SS[0:13] , DELT2[0:N,0:2,0:2],W[0:4,-4:4] ;
LABEL          ONE,WORK,EXIT1 ;
```

```
REAL PROCEDURE ACOS (X);
COMMENT, THIS PROCEDURE CALCULATES THE PRINCIPAL VALUE OF THE ARCCOS(X);
  VALUE          X;
  REAL           X ;
           BEGIN
REAL             A ;
                 IF X = 0 THEN
               A ← 0
               ELSE
                 A ← ARCTAN ((SQRT (1-X*2))/X);
               IF A < 0 THEN
               A ← 3.1415926536 + A ;
                 ACOS ← A
           END ;
PROCEDURE LEVEL3 (A,B,C,W,W1,W2) ;
VALUE            A,B,C ;
REAL             A,B,C ;
REAL ARRAY       W[0,-4],W1[0,-4,0],W2[0,-4,0,0] ;
                 BEGIN
INTEGER      I,J ;
REAL             R1,D10,D11,D12 ;
         W[0,2] := 5055310000 /C ;
         W1[0,2,2] := -5055310000 /C*2 ;
         W1[0,2,1] := 0 ;
         W1[0,2,0] := 0 ;
         FOR I := 0,1,2 DO FOR J := 0,1,2 DO
         W2[0,1,I,J] := W2[0,2,I,J] := 0 ;
         W2[0,2,2,2] := 10110620000 /C*3 ;
         W2[0,1,0,0] := 10110620000 /A*3 ;
         W2[0,1,1,1] := 10110620000 /B*3 ;
         W[0,1] := 5055310000 ×(1/A + 1/B ) ;
         W1[0,1,0] := -5055310000 /A*2 ;
         W1[0,1,1] := -5055310000 /B*2 ;
         W1[0,1,2] := 0 ;
         W[0,0] := 0 ;
```

```
FOR I := 0,1,2 DO BEGIN W1[0,0,I] := 0 ;
     FOR J := 0,1,2 DO W2[0,0,I,J] := 0 END;
W[1,-1] := B + C ;
W1[1,-1,0] := 0 ; W1[1,-1,1] := W1[1,-1,2] := 1 ;
FOR I := 0,1,2 DO FOR J := 0,1,2 DO W2[1,-1,I,J] := 0 ;
W[1, 0] := A + C ;
W1[1, 0,1] := 0 ; W1[1, 0,0] := W1[1, 0,2] := 1 ;
FOR I := 0,1,2 DO FOR J := 0,1,2 DO W2[1, 0,I,J] := 0 ;
W[1, 1] := A + B ;
W1[1, 1,2] := 0 ; W1[1, 1,0] := W1[1, 1,1] := 1 ;
FOR I := 0,1,2 DO FOR J := 0,1,2 DO W2[1, 1,I,J] := 0 ;
R1 := (B-C)*2 + (A-C) × (A-B) ;
D10 := 2 × A - B - C ;
D11 := 2 × B - A - C ;
D12 := 2 × C - A - B ;
W[2, 2] :=      2×(A+B+C+SQRT(R1)) ;
W1[2,2,0] := 2 + (D10/SQRT(R1)) ;
W1[2,2,1] := 2 + (D11/SQRT(R1)) ;
W1[2,2,2] := 2 + (D12/SQRT(R1)) ;
W2[2,2,0,0] := ( 2/SQRT(R1)) - .5× D10 × D10 / (R1 × SQRT(R1));
W2[2,2,0,1] := (-1/SQRT(R1)) - .5× D10 × D11 / (R1 × SQRT(R1));
W2[2,2,0,2] := (-1/SQRT(R1)) - .5× D10 × D12 / (R1 × SQRT(R1));
W2[2,2,1,1] := ( 2/SQRT(R1)) - .5× D11 × D11 / (R1 × SQRT(R1));
W2[2,2,1,2] := (-1/SQRT(R1)) - .5× D11 × D12 / (R1 × SQRT(R1));
W2[2,2,2,2] := ( 2/SQRT(R1)) - .5× D12 × D12 / (R1 × SQRT(R1));
FOR I := 1,2 DO FOR J := 0,1 DO W2[2,2,I,J] := W2[2,2,J,I] ;
W[2,-2] := 2×(A+B+C-SQRT(R1)) ;
W1[2,-2,0] := 2 - (D10 / SQRT (R1)) ;
W1[2,-2,1] := 2 - (D11 / SQRT (R1)) ;
W1[2,-2,2] := 2 - (D12 / SQRT (R1)) ;
FOR
I  := 0,1,2 DO FOR J := 0,1,2 DO W2[2,-2,I,J] := -W2[2,2,I,J] ;
W[2, 1] :=      4×A+B+C ;
W1[2, 1,0] := 4 ; W1[2, 1,1] := W1[2, 1,2] := 1 ;
FOR I := 0,1,2 DO FOR J := 0,1,2 DO W2[2, 1,I,J] := 0 ;
```

```
          W[2, 0] :=      A+4×B+C ;
          W1[2, 0,1] := 4 ; W1[2, 0,0] := W1[2, 0,2] := 1 ;
          FOR I := 0,1,2 DO FOR J := 0,1,2 DO W2[2, 0,I,J] := 0 ;
          W[2,-1] :=      A+B+4×C ;
          W1[2,-1,2] := 4 ; W1[2,-1,0] := W1[2,-1,1] := 1 ;
          FOR I := 0,1,2 DO FOR J := 0,1,2 DO W2[2,-1,I,J] := 0 ;
          R1  := 4×(A-B)*2 + (A-C)×(B-C) ;
          D10 := 8×A - 7×B - C ;
          D11 := 8×B - 7×A - C ;
          D12 := 2×C - B - A ;
          W[3, 3] := 5×(A+B) + 2×(C+SQRT(R1)) ;
          W1[3,3,0] := 5 + (D10/SQRT(R1)) ;
          W1[3,3,1] := 5 + (D11/SQRT(R1)) ;
          W1[3,3,2] := 5 + (D12/SQRT(R1)) ;
          W2[3,3,0,0] := ( 8/SQRT(R1)) - .5× D10 × D10 / (R1 × SQRT(R1)) ;
          W2[3,3,0,1] := (-7/SQRT(R1)) - .5× D10 × D11 / (R1 × SQRT(R1)) ;
          W2[3,3,0,2] := (-1/SQRT(R1)) - .5× D10 × D12 / (R1 × SQRT(R1)) ;
          W2[3,3,1,1] := ( 8/SQRT(R1)) - .5× D11 × D11 / (R1 × SQRT(R1)) ;
          W2[3,3,1,2] := (-1/SQRT(R1)) - .5× D11 × D12 / (R1 × SQRT(R1)) ;
          W2[3,3,2,2] := ( 2/SQRT(R1)) - .5× D12 × D12 / (R1 × SQRT(R1)) ;
          FOR I := 1,2 DO FOR J := 0,1 DO W2[3,3,I,J] := W2[3,3,J,I] ;
          W[3,-1] :=      2×(C-SQRT(R1)) + 5×(A+B) ;
          W1[3,-1,0] := 5 - (D10/SQRT(R1)) ;
          W1[3,-1,1] := 5 - (D11/SQRT(R1)) ;
          W1[3,-1,2] := 2 - (D12/SQRT(R1)) ;
          FOR
          I  := 0,1,2 DO FOR J := 0,1,2 DO W2[3,-1,I,J] := -W2[3,3,I,J] ;
          BEGIN
REAL      XXX ;
          R1 :=  4×(A-C)*2 - (A-B)×(B-C) ;
          D10 := 8×A - 7×C - B ;
          D11 := 2×B - C - A ;
          D12 := 8×C - 7×A - B ;
          W[3, 2] := 5×(B+C) + 2×(B+SQRT(R1)) ;
          W1[3,2,0] := 5 + (D10/SQRT(R1)) ;
```

```
W1[3,2,1] := 5 + (D11/SQRT(R1)) ;
W1[3,2,2] := 5 + (D12/SQRT(R1)) ;
W2[3,2,0,0] := ( 8/SQRT(R1)) - .5× D10 × D10 / (R1 × SQRT(R1));
W2[3,2,0,1] := (-1/SQRT(R1)) - .5× D10 × D11 / (R1 × SQRT(R1));
W2[3,2,0,2] := (-7/SQRT(R1)) - .5× D10 × D12 / (R1 × SQRT(R1));
W2[3,2,1,1] := ( 2/SQRT(R1)) - .5× D11 × D11 / (R1 × SQRT(R1));
W2[3,2,1,2] := (-1/SQRT(R1)) - .5× D11 × D12 / (R1 × SQRT(R1));
W2[3,2,2,2] := ( 8/SQRT(R1)) - .5× D12 × D12 / (R1 × SQRT(R1));
FOR I := 1,2 DO FOR J := 0,1 DO W2[3,2,I,J] := W2[3,2,J,I] ;
W[3,-2] :=     2×(B-SQRT(R1)) + 5×(A+C) ;
W1[3,-2,0] := 5 - (D10/SQRT(R1)) ;
W1[3,-2,1] := 2 - (D11/SQRT(R1)) ;
W1[3,-2,2] := 5 - (D12/SQRT(R1)) ;
FOR
I  := 0,1,2 DO FOR J := 0,1,2 DO W2[3,-2,I,J] := -W2[3,2,I,J] ;
R1  := 4×(B-C)*2 + (A-B)×(A-C) ;
D10 := 2×A - B - C ;
D11 := 8×B - 7×C - A ;
D12 := 8×C - 7×B - A ;
W[3, 1] := 2×(A+SQRT(R1)) + 5×(B+C) ;
W1[3,1,0] := 2 + (D10/SQRT(R1)) ;
W1[3,1,1] := 5 + (D11/SQRT(R1)) ;
W1[3,1,2] := 5 + (D12/SQRT(R1)) ;
W2[3,1,0,0] := ( 2/SQRT(R1)) - .5× D10 × D10 / (R1 × SQRT(R1));
W2[3,1,0,1] := (-1/SQRT(R1)) - .5× D10 × D11 / (R1 × SQRT(R1));
W2[3,1,0,2] := (-1/SQRT(R1)) - .5× D10 × D12 / (R1 × SQRT(R1));
W2[3,1,1,1] := ( 8/SQRT(R1)) - .5× D11 × D11 / (R1 × SQRT(R1));
W2[3,1,1,2] := (-7/SQRT(R1)) - .5× D11 × D12 / (R1 × SQRT(R1));
W2[3,1,2,2] := ( 8/SQRT(R1)) - .5× D12 × D12 / (R1 × SQRT(R1));
FOR I := 1,2 DO FOR J := 0,1 DO W2[3,1,I,J] := W2[3,1,J,I] ;
W[3,-3] :=     2×(A-SQRT(R1)) + 5×(B+C) ;
W1[3,-3,0] := 2 - (D10/SQRT(R1)) ;
W1[3,-3,1] := 5 - (D11/SQRT(R1)) ;
W1[3,-3,2] := 5 - (D12/SQRT(R1)) ;
FOR
```

```
I  := 0,1,2 DO FOR J := 0,1,2 DO W2[3,-3,I,J] := -W2[3,1,I,J] ;
W[3, 0] := 4×(A + B +C) ;
W1[3,0,0] := 4 ;
W1[3,0,1] := 4 ;
W1[3,0,2] := 4 ;
FOR I := 0,1,2 DO FOR J := 0,1,2 DO W2[3,0,I,J ] := 0 ;
R1  := 4×(B-C)*2 + 9×(A-C)×(A-B) ;
D10 := 18×A -9×C -9×B ;
D11 :=  8×B + C -9×A ;
D12 :=  8×C + B -9×A ;
W[4, 3] := 2×(5×A+SQRT(R1))+ 5×(B+C) ;
W1[4,3,0] := 10 + (D10/SQRT(R1)) ;
W1[4,3,1] :=  5 + (D11/SQRT(R1)) ;
W1[4,3,2] :=  5 + (D12/SQRT(R1)) ;
W2[4,3,0,0] := (18/SQRT(R1)) - .5× D10 × D10 / (R1 × SQRT(R1)) ;
W2[4,3,0,1] := (-9/SQRT(R1)) - .5× D10 × D11 / (R1 × SQRT(R1)) ;
W2[4,3,0,2] := (-9/SQRT(R1)) - .5× D10 × D12 / (R1 × SQRT(R1)) ;
W2[4,3,1,1] := ( 8/SQRT(R1)) - .5× D11 × D11 / (R1 × SQRT(R1)) ;
W2[4,3,1,2] := ( 1/SQRT(R1)) - .5× D11 × D12 / (R1 × SQRT(R1)) ;
W2[4,3,2,2] := ( 8/SQRT(R1)) - .5× D12 × D12 / (R1 × SQRT(R1)) ;
FOR I := 1,2 DO FOR J := 0,1 DO W2[4,3,I,J] := W2[4,3,J,I] ;
W[4,-1] := 2×(5×A-SQRT(R1))+ 5×(B+C) ;
W1[4,-1,0] := 10 - (D10/SQRT(R1)) ;
W1[4,-1,1] :=  5 - (D11/SQRT(R1)) ;
W1[4,-1,2] :=  5 - (D12/SQRT(R1)) ;
FOR
I  := 0,1,2 DO FOR J := 0,1,2 DO W2[4,-1,I,J] := -W2[4,3,I,J] ;
R1  := 4×(A-C)*2 - 9×(A-B)×(B-C) ;
D10 := 8×A + C - 9×B ;
D11 := 18×B - 9×C - 9×A ;
D12 := 8×C + A - 9×B ;
W[4, 2] := 5×(A+C) + 2×(5×B + SQRT(R1)) ;
W1[4,2,0] :=  5 + (D10/SQRT(R1)) ;
W1[4,2,1] := 10 + (D11/SQRT(R1)) ;
W1[4,2,2] :=  5 + (D12/SQRT(R1)) ;
```

```
W2[4,2,0,0] := ( 8/SQRT(R1)) - .5× D10 × D10 / (R1 × SQRT(R1))}
W2[4,2,0,1] := (-9/SQRT(R1)) - .5× D10 × D11 / (R1 × SQRT(R1))}
W2[4,2,0,2] := ( 1/SQRT(R1)) - .5× D10 × D12 / (R1 × SQRT(R1))}
W2[4,2,1,1] := (18/SQRT(R1)) - .5× D11 × D11 / (R1 × SQRT(R1))}
W2[4,2,1,2] := (-9/SQRT(R1)) - .5× D11 × D12 / (R1 × SQRT(R1))}
W2[4,2,2,2] := ( 8/SQRT(R1)) - .5× D12 × D12 / (R1 × SQRT(R1))}
FOR I := 1,2 DO FOR J := 0,1 DO W2[4,2,I,J] := W2[4,2,J,I] }
W[4,-2] := 2×(5×B-SQRT(R1))+ 5×(A+C) }
W1[4,-2,0] :=  5 - (D10/SQRT(R1)) }
W1[4,-2,1] := 10 - (D11/SQRT(R1)) }
W1[4,-2,2] :=  5 - (D12/SQRT(R1)) }
FOR
I  := 0,1,2 DO FOR J := 0,1,2 DO W2[4,-2,I,J] := -W2[4,2,I,J] }
R1  := 4×(A-B)*2 + 9×(A-C)×(B-C) }
D10 := 8×A + B - C }
D11 := 8×B + A - C }
D12 := 18×C - 9×B - 9×A }
W[4, 1] := 5×(A+B) + 2×(5×C + SQRT(R1)) }
W1[4,1,0] :=  5 + (D10/SQRT(R1)) }
W1[4,1,1] :=  5 + (D11/SQRT(R1)) }
W1[4,1,2] := 10 + (D12/SQRT(R1)) }
W2[4,1,0,0] := ( 8/SQRT(R1)) - .5× D10 × D10 / (R1 × SQRT(R1))}
W2[4,1,0,1] := ( 1/SQRT(R1)) - .5× D10 × D11 / (R1 × SQRT(R1))}
W2[4,1,0,2] := (-1/SQRT(R1)) - .5× D10 × D12 / (R1 × SQRT(R1))}
W2[4,1,1,1] := ( 8/SQRT(R1)) - .5× D11 × D11 / (R1 × SQRT(R1))}
W2[4,1,1,2] := (-1/SQRT(R1)) - .5× D11 × D12 / (R1 × SQRT(R1))}
W2[4,1,2,2] := (18/SQRT(R1)) - .5× D12 × D12 / (R1 × SQRT(R1))}
FOR I := 1,2 DO FOR J := 0,1 DO W2[4,1,I,J] := W2[4,1,J,I] }
W[4,-3] := 2×(5×C-SQRT(R1))+ 5×(A+B) }
W1[4,-3,0] :=  5 - (D10/SQRT(R1)) }
W1[4,-3,1] :=  5 - (D11/SQRT(R1)) }
W1[4,-3,2] := 10 - (D12/SQRT(R1)) }
FOR
I  := 0,1,2 DO FOR J := 0,1,2 DO W2[4,-3,I,J] := -W2[4,1,I,J] }
      END }
```

```
        BEGIN
REAL            BE,V,Q,D,H ; REAL ARRAY  DB,X[0:2],DDB[0:2,0:2] ;
INTEGER         K ;
                BE := (C-B)/(2×A-B-C) ;
                R1 := 64-208×BE*2 ;
                V := -400/3 + R1 ;
                Q := 2880 × BE*2 + 20×R1/3 - ((20*3)/13,5) ;
                D := 2×SQRT(-V/3) ;
                H := (ACOS((-Q/2)×SQRT(-27/V*3))) / 3 ;
                X[0] := D×COS(H) + (20/3) ;
                X[1] := D×COS(H + 2,0943951024) +(20/3) ;
                X[2] := D×COS(H + 4,1887902048) +(20/3) ;
                FOR I := 0,1,2 DO BEGIN K := -4 ; FOR J := 0,1,2 DO BEGIN
                IF X[I] > X[J] THEN K := K+4 END ; W[4,K] := X[I] END ;
        R1 := 2×A-B-C ;
        DB[0] := -2×BE / R1 ;
        DB[1] := (BE - 1)/R1 ;
        DB[2] := (BE + 1)/R1 ;
        DDB[0,0] := 8×BE/(R1*2) ;
        DDB[0,1] := -2×(2×BE - 1) / (R1*2) ;
        DDB[0,2] := -2×(2×BE + 1) / (R1*2) ;
        DDB[1,1] :=  2×(BE - 1) / (R1*2) ;
        DDB[1,2] :=  2×(BE - 0) / (R1*2) ;
        DDB[2,2] :=  2×(BE + 1) / (R1*2) ;
        R1 := 64 - 208 × BE*2 ;
        FOR I := 0,1 DO FOR J := 1,2 DO DDB[J,I] := DDB[I,J] ;
        FOR I := -4,0,4 DO FOR J := 0,1,2 DO
        W1[4,I,J] := BE×DB[J]×(5760 - 416×W[4,I])/
                     (3×W[4,I]*2 - 40×W[4,I] + R1) ;
        FOR K := -4,0,4 DO FOR I := 0,1,2 DO
        FOR J := I STEP 1 UNTIL 2 DO
        W2[4,K,I,J] := -((6×W[4,K]-40)×W1[4,K,I]×W1[4,K,J] -
                     416×BE×(DB[J]×W1[4,K,I] + DB[I]×W1[4,K,J]) +
        5344×(BE×DDB[I,J] + DB[I]×DB[J]))/(3×W[4,K]*2-40×W[4,K]+R1) ;
        FOR I := -4,0,4 DO BEGIN
```

```
          W2[4,K,0,0] := 2×W1[4,K,0] + A×W2[4,K,0,0] ;
          W2[4,K,0,1] := W1[4,K,1] + A×W2[4,K,0,1] ;
          W2[4,K,0,2] := W1[4,K,2] + A×W2[4,K,0,2] ;
          W2[4,K,1,1]  := -W1[4,K,1] - B×W2[4,K,1,1]/2 ;
          W2[4,K,1,2]  := -W1[4,K,2]/2 - B×W2[4,K,1,2]/2 ;
          W2[4,K,2,2]  := -W1[4,K,2]/2- C×W2[4,K,2,2]/2 END ;
          FOR K := -4,0,4 DO
          FOR I := 0,1 DO FOR J := 1,2 DO
          W2[4,K,J,I] := W2[4,K,I,J] ;
          FOR K := -4,0,4 DO BEGIN
          W1[4,K,0] := W[4,K] + A×W1[4,K,0] ;
          W1[4,K,1] := 10 - (W[4,K]/2) - B×W1[4,K,1]/2 ;
          W1[4,K,2] := 10 - (W[4,K]/2) - C×W1[4,K,2]/2  END ;
               FOR K := -4,0,4 DO W[4,K] := 10×(B+C)+(A-(B+C)/2)×W[4,K] ;
          END ;
               END ;
PROCEDURE      FREQ3 (N,JL,TL,JU,TU,A,B,C,FREQ,DF,DDF) ;
VALUE          N,A,B,C ;
INTEGER        N ;
REAL           A,B,C ;
INTEGER ARRAY  JL,TL,JU,TU[0] ;
REAL ARRAY     FREQ[0],DF[0,0],DDF[0,0,0] ;
          BEGIN
INTEGER        I,J,K ;
REAL ARRAY     W[0:4,-4:4],W1[0:4,-4:4,0:2],W2[0:4,-4:4,0:2,0:2] ;
               LEVEL3 (A,B,C,W,W1,W2) ;
               FOR I := 0 STEP 1 UNTIL N DO
                    BEGIN
               FREQ[I] := W[JU[I],TU[I]] - W[JL[I],TL[I]] ;
               FOR J := 0,1,2 DO
                    BEGIN
               DF[I,J] := W1[JU[I],TU[I],J] - W1[JL[I],TL[I],J] ;
               FOR K := 0,1,2 DO
                     BEGIN
               DDF[I,J,K] := W2[JU[I],TU[I],J,K] - W2[JL[I],TL[I],J,K] ;
```

```
                END END END END ;
REAL ARRAY      CS[0:N] ;
FORMAT OUT      FMO1 (X48,4A6),
                FMO2 (X24,"A",X17,"B",X17,"C",X13,"SUM OF SQUARES",/
                X15,  3F18.9,E23.12,F9.4),
                FMO3 (X21,"J   TAU     J   TAU   EXP. FREQ.",X12,
                "CALC. FREQ.",X15,"DIFF."/(X15,2(X2,2I5),F13.3,X9,
                F18.8,X4,F14.5)//) ;
LIST            OUT1 (FOR K ← 0 STEP 1 UNTIL 3 DO NAME[K]),
                OUT2 (A[0],A[1],A[2],S,TT),
                OUT3 (FOR J ← 0 STEP 1 UNTIL N DO
                   [JL[J],TL[J],JU[J],TU[J],NU[J],NUC[J],NU[J]-NUC[J]]) ;
WORK:
                              BEGIN
                M ← M + 1 ;
                FREQ3 (N,JL,TL,JU,TU,A[0],A[1],A[2],NUC,DELT,DELT2) ;
                SUM ← 0 ;
                FOR J ← 0 STEP 1 UNTIL N DO
                SUM ← SUM + (NU[J] - NUC[J]) * 2 ;
                IF M = 1 THEN S ← SUM + 0.1 ;
                DS ← SUM - S ;
                S ← SUM ;
                WRITE (FO1,FMO1,OUT1) ;
                WRITE (FO1[DBL]) ;
                WRITE (FO1,FMO2,OUT2) ;
                WRITE (FO1[DBL]) ;
                WRITE (FO1,FMO3,OUT3) ;
                WRITE (FO1[DBL]) ;
                WRITE (FO1[DBL]) ;
                WRITE (FO1[DBL]) ;
                WRITE (FO1[DBL]) ;
                IF ((M = M1) OR (DS = 0)) THEN GO TO EXIT1 ;
                FOR I ← 0 STEP 1 UNTIL 2 DO
                FOR J ← 0 STEP 1 UNTIL 2 DO
                              BEGIN
```

```
SUM ← 0 ;
FOR K ← 0 STEP 1 UNTIL N DO
SUM := SUM
+  DELT[K,J]×DELT[K,I]-(NU[K]-NUC[K])×DELT2[K,I,J] ;
X[I,J] ← SUM
                  END ;
FOR I ← 0 STEP 1 UNTIL 2 DO
     BEGIN
X[I,3] := 0 ;
FOR J := 0 STEP 1 UNTIL N DO
X[I,3] := X[I,3] +(NU[J] - NUC[J]) × DELT[J,I]
     END ;
     BEGIN
FOR K ← 2 STEP -1 UNTIL 0 DO
          BEGIN
FOR J ← 0 STEP 1 UNTIL K DO
DA[J] ← X[0,J+1] / X[0,0] ;
FOR I ← 0,1 DO
FOR J ← 0 STEP 1 UNTIL K DO
X[I,J] ← X[I+1,J+1] - X[I+1,0] × DA[J] ;
FOR J ← 0 STEP 1 UNTIL K DO
X[2,J] ← DA[J]
          END ;
FOR I ← 0 STEP 1 UNTIL 2 DO
DA[I] ← X[I,0]
     END ;
FOR I ← 0 STEP 1 UNTIL 13 DO
     BEGIN
T[I] ← -1.75 + 0.25 × I ;
FOR J ← 0 STEP 1 UNTIL 2 DO
A[J] ← A[J] + DA[J] × T[I] ;
SS[I] := 0 ;
FREQ3(N,JL,TL,JU,TU,A[0],A[1],A[2],CS,DELT,DELT2) ;
FOR K ← 0 STEP 1 UNTIL N DO
SS[I] := SS[I] + (NU[K] - CS[K])*2 ;
```

```
                FOR J ← 0 STEP 1 UNTIL 2 DO
                A[J] ← A[J] - DA[J] × T[I] ;
                     END ;
                K ← 999 ;
                FOR I ← 0 STEP 1 UNTIL 13 DO
                          BEGIN
                R ← 1 ;
                FOR J ← 0 STEP 1 UNTIL 13 DO
                IF SS[I] > SS[J] THEN R ← R + 1 ;
                K ← R ;
                IF K = 1 THEN
                                  BEGIN
                IF I ≠ 7 THEN
                                       BEGIN
                TT ← T[I] ;
                GO TO ONE
                                       END
                ELSE
                TT := 0.5×((SS[I+1]-SS[I])×(T[I-1]+T[I])+(SS[I-1]-SS[I])×
                     (T[I+1]+T[I]))/((SS[I-1]-SS[I])+(SS[I+1]-SS[I])) ;
                GO TO ONE
                                  END
                          END ;
ONE:            FOR R ← 0 STEP 1 UNTIL 2 DO
                A[R] ← A[R] + TT×DA[R] ;
                GO TO WORK ;
EXIT1:                            END
                     END
                END
          END .
?30         END-OF-FILE CARD                                          ?
 LABEL   000000000FI1     0010000001
```

SAMPLE DATA CARDS

```
S CL  CL 35,35 J≤4 CD COR
   7    5    14613.3556      2920.9256      2430.7415
  0    0        1    0    17044.2192
  2 -02        2    0    12687.9471
  2 - 2        3 - 2     26527.9513
  3 - 2        4 - 4     10723.2575
  4 - 2        3    0    11995.4928
  4 - 2        4    0    33615.8721
  4 - 4        4 - 2     14573.2514
```

END OF SAMPLE DATA CARDS

```
?31          END-OF-DECK-CARD
```

?

Sample Problem Output

Oxygen Difluoride $J \leq 4$

A	B	C	SUM OF SQUARES	
58782.630000000	10896.431000000	9167.412000000	3.469749722470@+02	0.0000

J	TAU	J	TAU	EXP. FREQ.	CALC. FREQ.	DIFF.
1	-1	1	1	49613.550	49615.21800040	-1.66800
2	-2	2	0	51388.950	51390.21789980	-1.26790
3	-3	3	-1	54137.050	54138.32357500	-1.27357
2	-1	3	-3	13804.030	13804.66083050	-0.63083
4	-4	4	-2	57958.300	57959.92480100	-1.62480
3	-2	4	-4	36028.730	36032.53953700	-3.80954
4	-2	3	0	57457.100	57475.08367800	-17.98368

A	B	C	SUM OF SQUARES	
58774.128677000	10895.613432200	9164.947874400	5.342119179050@+01	1.0000

J	TAU	J	TAU	EXP. FREQ.	CALC. FREQ.	DIFF.
1	-1	1	1	49613.550	49609.18080330	4.36920
2	-2	2	0	51388.950	51385.92133810	3.02866
3	-3	3	-1	54137.050	54136.81220720	0.23779
2	-1	3	-3	13804.030	13803.67659000	0.35341
4	-4	4	-2	57958.300	57962.44356200	-4.14356
3	-2	4	-4	36028.730	36029.86853410	-1.13853
4	-2	3	0	57457.100	57459.65180600	-2.55181

A	B	C	SUM OF SQUARES	
58774.676635000	10895.74163600	9165.349234800	4.966132957870@+01	1.0000

J	TAU	J	TAU	EXP. FREQ.	CALC. FREQ.	DIFF.
1	-1	1	1	49613.550	49609.32740020	4.22260
2	-2	2	0	51388.950	51385.77997350	3.17003
3	-3	3	-1	54137.050	54136.21146440	0.83854
2	-1	3	-3	13804.030	13804.64626880	-0.61627
4	-4	4	-2	57958.300	57961.18045500	-2.88045
3	-2	4	-4	36028.730	36031.09577700	-2.36578
4	-2	3	0	57457.100	57459.70865200	-2.60865

APPENDIX B

THE MEASURED SPECTRUM OF $S^{32}Cl_2{}^{35}$

APPENDIX B

THE MEASURED SPECTRUM OF $S^{32}Cl_2{}^{35}$

This appendix presents in Table 11 the rotational transitions in the microwave spectrum of sulfur dichloride which have been measured in this investigation. The hyperfine splittings measured in the study of the electric quadrupole coupling are presented in Table 12. In these tables the experimental data are compared with values calculated using the molecular parameters given in Chapter V.

The rotational spectrum was calculated by diagonalization of energy matrices using the methods described in Appendix A.

Quadrupole coupling frequency shifts were calculated using the methods described in Chapter III. The functions $A(J, \tau)$ and $B(J,\tau)$ were calculated using the closed form expressions given by Clayton (89) and the present author (Appendix D) where possible. In the case of levels for which there exist no closed form expressions $A(J, \tau)$ and $B(J, \tau)$ were evaluated by linear interpolation in the reduced energy tables of Nolan et al. (90) and using the expressions given in Equation (19).

Table 11. The Measured Rotational Spectrum of $S^{32}Cl_2{}^{35}$*

Transition $J_\tau \rightarrow J'_{\tau'}$		Theoretical Relative Intensity	Measured Frequency $\nu_o{}^m$	Calculated Frequency $\nu_o{}^c$	$\nu_o{}^m - \nu_o{}^c$
0_o	1_o	1.0	17044.17	17044.01	0.16
1_{-1}	1_1	1.5	12182.96	12182.62	0.34
2_{-2}	2_o	2.5	12687.96	12687.88	0.08
2_{-2}	3_{-2}	2.0	26527.85	26527.49	0.36
3_{-3}	3_{-1}	3.5	13473.95	13473.82	0.13
3_{-2}	4_{-4}	1.5	10722.38	10723.07	-0.69
4_{-2}	3_o	0.4	11995.82	11996.21	-0.39
4_{-2}	4_o	2.0	33615.96	33616.08	-0.12
4_{-4}	4_{-2}	4.5	14573.26	14573.14	0.12
4_{-4}	5_{-4}	3.0	35143.14	35142.79	0.35
5_{-5}	5_{-3}	5.5	16027.02	16027.00	0.02
5_{-4}	4_o	0.6	13046.04	13046.43	-0.39
6_{-6}	6_{-4}	6.5	17881.09	17881.54	-0.43
7_{-7}	7_{-5}	7.5	20181.33	20182.23	-0.90
8_{-8}	8_{-6}	8.5	22964.78	22966.60	-1.82
12_{-10}	12_{-8}	6.2	31088.85	31088.82	0.03
14_{-8}	15_{-12}		9712.0	9716.8	-4.8 **

*Calculated frequencies based on A = 14613.32 Mc, B = 2920.861 Mc, and C = 2430.692 Mc.

**This is a doubtful assignment.

Table 12. Measured Hyperfine Splittings in $S^{32}Cl_2{}^{35}$

Transition						Theoretical Relative Intensity	Calculated Quadrupole Splittings $\Delta \nu^c$	Measured Quadrupole Splittings $\Delta \nu^m$	$\Delta \nu^m - \Delta \nu^c$
J_τ	$\rightarrow J'_{\tau'}$	ϵ	F	$\rightarrow \epsilon'$	F'		(Mc)	(Mc)	(Mc)
0_0	1_0	0	0	0	1	1.00	- 2.82	- 2.88	- 0.06*
		2	2	2	3	2.33	0.0	0.0	0.0
		2	2	2	2	0.55	0.0	0.0	0.0
		2	2	2	1	1.00	2.82	2.92	0.10*
		0	0	2	1	0.00	2.82	2.92	0.10*
1_{-1}	1_1	1	2	1	2	0.70	-31.55	...	...
		1	1	1	2	0.10	-25.17	-24.82	0.35
		1	2	1	1	0.10	-23.70	-23.81	- 0.11
		1	1	1	1	0.25	-17.31	-17.38	- 0.07
		3	2	1	2	0.02	-11.02	-10.82	0.20
		3	4	3	4	1.88	- 8.66	- 8.64	0.02
		1	2	3	2	0.02	- 6.29	...	...
		3	3	1	2	0.85	- 5.76	- 5.73	0.03
		3	2	1	1	0.32	- 3.16	- 3.25	- 0.09
		1	1	3	2	0.32	0.10	0.24	---
		1	2	3	3	0.85	0.17	0.24	---
		1	0	1	1	0.33	5.98	5.99	0.01
		3	3	3	4	1.13	6.87	6.72	- 0.15
		3	4	3	3	1.13	10.44	10.50	0.06
		1	1	1	0	0.33	11.33	...	...
		3	2	3	2	1.07	14.24	14.19	- 0.05
		3	3	3	2	0.26	19.50	19.47	- 0.03
		3	2	3	3	0.26	20.71	...	...
		3	3	3	3	0.10	25.96	...	...

---This is an unresolved group of lines.

Table 12. Measured Hyperfine Splittings in $S^{32}Cl_2^{35}$ (Continued)

Transition						Theoretical Relative Intensity	Calculated Quadrupole Splittings $\Delta \nu^c$	Measured Quadrupole Splittings $\Delta \nu^m$	$\Delta \nu^m - \Delta \nu^c$
J_τ	$J'_{\tau'}$	ϵ	F	ϵ'	F'		(Mc)	(Mc)	(Mc)
2_{-2}	2_0	2	2	2	2	0.56	-13.06	-12.96	0.10*
		2	2	2	3	0.20	-10.68	...	...
		2	2	2	1	0.18	-10.68	...	...
		2	2	0	2	0.06	- 8.29	...	...
		2	1	2	2	0.18	- 2.39	- 2.38	0.01*
		2	3	2	2	0.20	- 2.39	- 2.38	0.01*
		2	4	2	4	1.50	0.00	0.00	0.00
		2	3	2	3	0.70	0.00	0.00	0.00
		2	1	2	1	0.05	0.00	0.00	0.00
		2	0	2	0	0.00	0.00	0.00	0.00
		2	3	2	4	0.30	0.00	0.00	0.00
		2	4	2	5	0.20	0.00	0.00	0.00
		2	4	2	3	0.30	0.00	0.00	0.00
		2	1	2	0	0.20	0.00	0.00	0.00
		2	1	0	2	0.18	2.39	...	...
		2	3	0	2	0.20	2.39	...	...
		0	2	2	2	0.06	8.29	8.58	0.29*
		0	2	2	1	0.18	10.68	10.80	0.12*
		0	2	2	3	0.20	10.68	10.80	0.12*
		0	2	0	2	0.56	13.06	13.18	0.12*

...These transitions were not measured because of low intensity of the lines or interference.

Table 12. Measured Hyperfine Splittings to $S^{32}Cl_2{}^{35}$ (Continued)

Transition						Theoretical Relative Intensity	Calculated Quadrupole Splittings $\Delta \nu^c$	Measured Quadrupole Splittings $\Delta \nu^m$	$\Delta \nu^m - \Delta \nu^c$
J_τ	$\rightarrow J'_{\tau'}$	ϵ	F	$\rightarrow \epsilon'$	F'		(Mc)	(Mc)	(Mc)
2_{-2}	3_{-2}	2	2	0	3	0.01	-25.81	...	...
		2	3	0	3	0.15	-15.02	...	...
		2	4	0	3	0.01	-15.02	...	...
		2	2	2	2	0.14	-10.79	...	...
		2	2	2	1	0.01	-10.79	...	...
		0	2	0	3	0.84	- 4.24	- 4.33	-0.09*
		2	4	2	5	1.57	0.00	0.00	0.00
		2	3	2	4	1.07	0.00	0.00	0.00
		2	1	2	2	0.40	0.00	0.00	0.00
		2	0	2	1	0.20	0.00	0.00	0.00
		2	4	2	4	0.21	0.00	0.00	0.00
		2	1	2	1	0.20	0.00	0.00	0.00
		2	3	2	2	0.03	0.00	0.00	0.00
		2	2	2	3	0.84	4.24	4.22	-0.02*
		0	2	2	2	0.14	10.79	...	...
		0	2	2	1	0.01	10.79	...	...
		2	3	2	3	0.15	15.02	...	...
		2	4	2	3	0.01	15.02	...	...
		0	2	2	3	0.01	25.81	...	...

Table 12. Measured Hyperfine Splittings to $S^{32}Cl_2^{35}$ (Continued)

Transition						Theoretical Relative Intensity	Calculated Quadrupole Splittings $\Delta\nu^c$	Measured Quadrupole Splittings $\Delta\nu^m$	$\Delta\nu^m - \Delta\nu^c$
J_τ	$J'_{\tau'}$	ϵ	F	ϵ'	F'		(Mc)	(Mc)	(Mc)
3_{-3}	3_{-1}	3	0	3	1	0.14	-16.32	...	...
		3	0	3	0	0.00	-16.20	...	...
		3	1	1	2	0.02	-12.70	-12.36	---
		3	1	3	2	0.25	-12.33	-12.36	---
		3	1	3	1	0.02	-12.15	-12.36	---
		3	1	3	0	0.14	-12.04	-12.36	---
		1	3	3	4	0.00	-11.22	-10.67	---
		1	3	1	2	0.04	-11.07	-10.67	---
		1	3	3	3	0.02	-11.02	-10.67	---
		1	3	1	4	0.13	-10.83	-10.67	---
		1	3	3	2	0.09	-10.70	-10.67	---
		1	3	1	3	0.72	-10.58	-10.67	---
		3	6	3	5	0.23	- 7.13	- 6.75	---
		3	6	3	6	1.62	- 6.75	- 6.75	---
		3	2	1	2	0.01	- 6.35	- 6.75	---
		3	2	3	3	0.25	- 6.29	- 6.75	---
		3	2	3	2	0.11	- 5.98	- 6.75	---
		3	2	1	3	0.09	- 5.85	- 6.75	---
		3	2	3	1	0.25	- 5.80	- 6.75	---
		1	4	3	4	0.03	- 1.87	- 1.48	---
		1	4	3	5	0.11	- 1.72	- 1.48	---
		1	4	3	3	0.05	- 1.67	- 1.48	---
		1	4	1	4	0.97	- 1.48	- 1.48	---
		1	4	1	3	0.13	- 1.23	- 1.48	---

Table 12. Measured Hyperfine Splittings to $S^{32}Cl_2^{35}$ (Continued)

Transition $J_\tau \rightarrow J'_{\tau'}$	ϵ	F	$\rightarrow$	ϵ'	F'	Theoretical Relative Intensity	Calculated Quadrupole Splittings $\Delta \nu^c$ (Mc)	Measured Quadrupole Splittings $\Delta \nu^m$ (Mc)	$\Delta \nu^m - \Delta \nu^c$ (Mc)
	3	3		3	4	0.29	4.97	5.22	---
	3	3		1	2	0.06	5.11	5.22	---
	3	3		3	3	0.32	5.17	5.22	---
	3	3		1	4	0.05	5.36	5.22	---
	3	3		3	2	0.25	5.48	5.22	---
	3	3		1	3	0.02	5.61	5.22	---
	3	5		3	4	0.25	6.60	6.81	---
	3	5		3	5	0.98	6.75	6.81	---
	3	5		1	4	0.11	6.98	6.81	---
	3	5		3	6	0.23	7.13	...	...
	1	2		1	2	0.58	7.32	...	...
	1	2		3	3	0.06	7.38	...	...
	1	2		3	2	0.01	7.70	...	...
	1	2		1	3	0.04	7.83	...	...
	1	2		3	1	0.02	7.87	...	...
	3	4		3	4	0.71	12.29	12.29	---
	3	4		3	5	0.25	12.44	12.29	---
	3	4		3	3	0.29	12.49	12.29	---
	3	4		1	4	0.03	12.67	12.29	---
	3	4		1	3	0.00	12.93	12.29	---

Table 12. Measured Hyperfine Splittings to $S^{32}Cl_2^{35}$ (Continued)

Transition						Theoretical Relative Intensity	Calculated Quadrupole Splittings $\Delta \nu^c$	Measured Quadrupole Splittings $\Delta \nu^m$	$\Delta \nu^m - \Delta \nu^c$
J_τ	$\rightarrow J'_{\tau'}$	ϵ	F	$\rightarrow \epsilon'$	F'		(Mc)	(Mc)	(Mc)
3_{-2}	4_{-4}	2	3	0	4	0.00	-26.30	...	...
		2	3	2	3	0.09	-15.02	...	...
		2	3	2	2	0.00	-15.02	...	...
		2	4	0	4	0.09	-11.28	...	...
		2	5	0	4	0.00	-11.28	...	...
		2	3	2	4	0.91	- 3.74	-3.67	0.07*
		2	4	2	6	1.44	0.00	0.00	0.00
		2	4	2	5	1.10	0.00	0.00	0.00
		2	2	2	3	0.60	0.00	0.00	0.00
		2	1	2	2	0.43	0.00	0.00	0.00
		2	5	2	5	0.12	0.00	0.00	0.00
		2	2	2	2	0.12	0.00	0.00	0.00
		2	4	2	3	0.01	0.00	0.00	0.00
		0	3	0	4	0.91	3.74	3.63	-0.11*
		2	4	2	4	0.09	11.28	...	...
		2	5	2	4	0.00	11.28	...	...
		0	3	2	3	0.09	15.02	...	...
		0	3	2	2	0.00	15.02	...	...
		0	3	2	4	0.00	26.30	...	...

Table 12. Measured Hyperfine Splittings in $S^{32}Cl_2^{35}$ (Continued)

Transitions						Theoretical Relative Intensity	Calculated Quadrupole Splittings $\Delta \nu^c$	Measured Quadrupole Splittings $\Delta \nu^m$	$\Delta \nu^m - \Delta \nu^c$
J_τ	$\rightarrow J'_{\tau'}$	ϵ	F	$\rightarrow \epsilon'$	F'				
							(Mc)	(Mc)	(Mc)
4_{-2}	3_0	2	4	2	3	0.91	-1.42	-1.37	0.05*
		2	4	2	4	0.09	-1.42	-1.37	0.05*
		2	4	2	5	0.00	-1.42	-1.37	0.05*
		2	4	0	3	0.00	-1.42	-1.37	0.05*
		2	6	2	5	1.44	0.00	0.00	0.00
		2	5	2	4	1.10	0.00	0.00	0.00
		2	3	2	2	0.60	0.00	0.00	0.00
		2	2	2	1	0.43	0.00	0.00	0.00
		2	5	2	5	0.12	0.00	0.00	0.00
		2	3	2	3	0.09	0.00	0.00	0.00
		2	2	2	2	0.12	0.00	0.00	0.00
		2	3	2	4	0.01	0.00	0.00	0.00
		2	2	2	3	0.00	0.00	0.00	0.00
		2	3	0	3	0.09	0.00	0.00	0.00
		2	2	0	3	0.00	0.00	0.00	0.00
		0	4	0	3	0.91	1.42	1.39	-0.03*
		0	4	2	3	0.00	1.42	1.39	-0.03*
		0	4	2	4	0.09	1.42	1.39	-0.03*
		0	4	2	5	0.00	1.42	1.39	-0.03*

Table 12. Measured Hyperfine Splittings in $S^{32}Cl_2^{35}$ (Continued)

Transition $J_\tau \rightarrow J'_{\tau'}$	ϵ	F	$\rightarrow$	ϵ'	F'	Theoretical Relative Intensity	Calculated Quadrupole Splittings $\Delta\nu^c$	Measured Quadrupole Splittings $\Delta\nu^m$	$\Delta\nu^m - \Delta\nu^c$
							(Mc)	(Mc)	(Mc)
$4_{-4} \quad 4_{-2}$	2	4		0	4	0.01	-12.60	...	...
	2	4		2	5	0.07	-11.18	-11.01	0.17*
	2	4		2	3	0.07	-11.18	-11.01	0.17*
	2	4		2	4	0.86	- 9.76	- 9.60	0.16*
	2	3		0	4	0.07	- 1.42	- 1.28	0.14*
	2	5		0	4	0.07	- 1.42	- 1.28	0.14*
	2	6		2	6	1.35	0.00	0.00	0.00
	2	5		2	5	0.99	0.00	0.00	0.00
	2	3		2	3	0.55	0.00	0.00	0.00
	2	2		2	2	0.46	0.00	0.00	0.00
	2	5		2	6	0.10	0.00	0.00	0.00
	2	2		2	3	0.09	0.00	0.00	0.00
	2	6		2	5	0.10	0.00	0.00	0.00
	2	3		2	2	0.09	0.00	0.00	0.00
	2	3		2	4	0.07	1.42	1.30	-0.12*
	2	5		2	4	0.07	1.42	1.30	-0.12*
	0	4		0	4	0.86	9.76	9.82	0.06*
	0	4		2	3	0.07	11.18	11.14	-0.04*
	0	4		2	5	0.07	11.18	11.14	-0.04*
	0	4		2	4	0.01	12.60	...	...

Table 12. Measured Hyperfine Splittings in $S^{32}Cl_2{}^{35}$ (Continued)

Transition $J_\tau \rightarrow J'_{\tau'}$	ϵ F $\rightarrow$ ϵ' F'	Theoretical Relative Intensity	Calculated Quadrupole Splittings $\Delta\nu^c$	Measured Quadrupole Splittings $\Delta\nu^m$	$\Delta\nu^m - \Delta\nu^c$
			(Mc)	(Mc)	(Mc)
5_{-4} 4_0	0 5 2 4	0.00	-19.12	...	...
	0 5 2 5	0.06	-16.40	-16.44	-0.04
	0 5 2 6	0.01	-16.40	-16.44	-0.04
	0 5 0 4	0.93	-13.67	-13.75	-0.08
	2 4 2 4	0.05	- 2.73	...	...
	2 3 2 4	0.00	- 2.73	...	...
	2 7 2 6	1.37	0.00	0.00	0.00
	2 6 2 5	1.10	0.00	0.00	0.00
	2 4 2 3	0.68	0.00	0.00	0.00
	2 3 2 2	0.53	0.00	0.00	0.00
	2 6 2 6	0.08	0.00	0.00	0.00
	2 3 2 3	0.09	0.00	0.00	0.00
	2 4 2 5	0.00	0.00	0.00	0.00
	2 4 0 4	0.05	2.73	...	...
	2 3 0 4	0.00	2.73	...	...
	2 5 2 4	0.93	13.67	13.64	-0.03
	2 5 2 5	0.06	16.40	16.50	0.10
	2 5 2 6	0.01	16.40	16.50	0.10
	2 5 0 4	0.00	19.12	...	...

Table 12. Measured Hyperfine Splittings in $S^{32}Cl_2^{35}$ (Continued)

Transition $J_\tau \rightarrow J'_{\tau'}$	ϵ F $\rightarrow$ ϵ' F'	Theoretical Relative Intensity	Calculated Quadrupole Splittings $\Delta \nu^c$	Measured Quadrupole Splittings $\Delta \nu^m$	$\Delta \nu^m - \Delta \nu^c$
			(Mc)	(Mc)	(Mc)
$5_{-5} \rightarrow 5_{-3}$	1 5 → 3 6	0.00	-14.29	...	...
	3 2 → 3 3	0.09	-14.16	...	...
	1 5 → 3 5	0.00	-13.50	...	...
	1 5 → 1 4	0.01	-13.37	...	...
	3 2 → 3 2	0.34	-12.78	-12.79	-0.01
	1 5 → 1 6	0.06	-11.68	...	...
	1 5 → 3 4	0.07	-11.44	...	...
	3 8 → 3 7	0.10	- 9.92	- 9.84	---
	1 5 → 1 5	0.88	- 9.72	- 9.84	---
	3 3 → 1 4	0.02	- 9.32	- 9.84	---
	3 3 → 3 4	0.12	- 7.39	- 7.35	---
	3 8 → 3 8	1.46	- 7.37	- 7.35	---
	3 3 → 3 3	0.32	- 6.39	- 6.30	0.09
	3 3 → 3 2	0.09	- 5.01	...	...
	3 4 → 3 5	0.11	- 3.81	...	...
	1 6 → 3 6	0.01	- 3.24	...	...
	1 6 → 3 5	0.05	- 2.44	...	...
	3 4 → 3 4	0.52	- 1.75	- 1.76	---
	1 6 → 3 7	0.08	- 1.72	- 1.76	---
	3 4 → 3 3	0.12	- 0.75	...	...
	1 6 → 1 6	1.04	- 0.63	- 0.63	-0.00
	3 4 → 1 5	0.07	- 0.03	...	...

Table 12. Measured Hyperfine Splittings in $S^{32}Cl_2^{35}$ (Continued)

Transition $J_\tau \rightarrow J'_{\tau'}$ ϵ F $\rightarrow$ ϵ' F'	Theoretical Relative Intensity	Calculated Quadrupole Splittings $\Delta \nu^c$	Measured Quadrupole Splittings $\Delta \nu^m$	$\Delta \nu^m - \Delta \nu^c$
		(Mc)	(Mc)	(Mc)
3 4 1 6	0.01	0.59	...	...
1 6 1 5	0.06	1.33	...	...
3 7 3 6	0.12	2.91	...	...
3 7 3 7	1.10	4.42	4.43	0.01
3 7 1 6	0.08	5.52	...	...
3 5 3 6	0.15	6.96	7.61	---
3 7 3 8	0.10	6.97	7.61	---
1 4 3 5	0.06	7.04	7.61	---
1 4 1 4	0.71	7.16	7.70	---
3 5 3 5	0.65	7.76	7.70	---
3 5 1 4	0.06	7.88	7.70	---
1 4 3 4	0.01	9.09	...	...
3 5 1 6	0.05	9.57	...	...
3 5 3 4	0.11	9.81	...	...
1 4 3 4	0.02	10.09	...	...
1 4 1 5	0.01	10.81	...	...
3 6 3 6	0.91	11.45	11.41	-0.04
3 5 1 5	0.00	11.53	...	...
3 6 3 5	0.15	12.25	...	...
3 6 3 7	0.12	12.97	...	...
3 6 1 6	0.01	14.06	...	...
3 6 1 5	0.00	16.02	...	...

Table 12. Measured Hyperfine Splittings in $S^{32}Cl_2^{35}$ (Continued)

Transition				Theoretical Relative Intensity	Calculated Quadrupole Splittings $\Delta \nu^c$	Measured Quadrupole Splittings $\Delta \nu^m$	$\Delta \nu^m - \Delta \nu^c$
J_τ	$J'_{\tau'}$	ϵ F	ϵ' F'		(Mc)	(Mc)	(Mc)
6_{-6}	6_{-4}	2 6	0 6	0.00	-15.16	...	...
		2 6	2 7	0.03	-12.55	-12.58	0.03
		2 6	2 5	0.03	-12.55	-12.58	0.03
		2 6	2 6	0.93	- 9.95	- 9.87	0.08
		2 5	0 6	0.03	- 2.61	- 2.38	0.23
		2 7	0 6	0.03	- 2.61	- 2.38	0.23
		2 8	2 8	1.26	0.00	0.00	0.00
		2 7	2 7	1.04	0.00	0.00	0.00
		2 5	2 5	0.73	0.00	0.00	0.00
		2 4	2 4	0.65	0.00	0.00	0.00
		2 7	2 8	0.05	0.00	0.00	0.00
		2 4	2 5	0.05	0.00	0.00	0.00
		2 8	2 7	0.05	0.00	0.00	0.00
		2 5	2 4	0.05	0.00	0.00	0.00
		2 5	2 6	0.03	2.61	...	...
		2 7	2 6	0.03	2.61	...	...
		0 6	0 6	0.93	9.95	10.13	0.08
		0 6	2 5	0.03	12.55	12.62	-0.07
		0 6	2 7	0.03	12.55	12.62	-0.07
		0 6	2 6	0.00	15.16	...	...

Table 12. Measured Hyperfine Splittings in $S^{32}Cl_2{}^{35}$ (Continued)

Transition						Theoretical Relative Intensity	Calculated Quadrupole Splittings $\Delta \nu^c$	Measured Quadrupole Splittings $\Delta \nu^m$	$\Delta \nu^m - \Delta \nu^c$
J_τ	$\rightarrow$	$J'_{\tau'}$	ϵ F	$\rightarrow$	ϵ' F'		(Mc)	(Mc)	(Mc)
7_{-7}		7_{-5}	1 7		1 6	0.00	-15.83	...	...
			3 4		3 5	0.05	-14.96	...	...
			1 7		1 8	0.02	-13.28	-12.64	---
			3 4		3 4	0.50	-12.61	-12.64	---
			3 10		3 9	0.05	-12.03	-12.64	---
			1 7		1 7	0.95	-10.32	-10.35	-0.03
			3 10		3 10	1.25	- 8.44	- 8.49	-0.05
			3 5		3 6	0.05	- 5.88	- 4.77	---
			3 5		3 5	0.60	- 4.73	- 4.77	---
			3 6		3 7	0.05	- 3.85	...	...
			3 5		3 4	0.04	- 2.38	...	...
			3 6		3 6	0.70	- 0.86	- 0.45	---
			1 8		1 8	1.06	- 0.40	- 0.45	---
			3 6		3 5	0.04	0.30	- 0.45	---
			3 9		3 8	0.04	1.15	...	...
			1 8		1 7	0.02	2.56	2.22	-0.24
			3 9		3 9	1.11	3.62	3.64	0.02
			3 9		3 10	0.03	7.21	...	...
			1 6		1 6	0.80	8.18	8.24	---
			3 7		3 8	0.05	8.41	8.24	---
			3 7		3 7	0.80	9.21	9.20	-0.01
			3 8		3 8	1.00	11.90	11.95	---
			3 7		3 6	0.05	12.20	11.95	---
			3 8		3 7	0.05	12.70	11.95	---
			1 6		1 7	0.00	13.69	13.75	0.06
			3 8		3 9	0.05	14.36	...	...

Table 12. Measured Hyperfine Splittings in $S^{32}Cl_2{}^{35}$ (Concluded)

Transition $J_\tau \rightarrow J'_{\tau'}$	ϵ F	ϵ' F'	Theoretical Relative Intensity	Calculated Quadrupole Splittings $\Delta\nu^c$	Measured Quadrupole Splittings $\Delta\nu^m$	$\Delta\nu^m - \Delta\nu^c$
				(Mc)	(Mc)	(Mc)
$8_{-8} \quad 8_{-6}$	2 8	0 8	0.00	-17.80	...	...
	2 8	2 9	0.01	-14.26	...	...
	2 8	2 7	0.01	-14.26	...	...
	2 8	2 8	0.95	-10.73	-10.83	-0.10
	2 7	0 8	0.00	- 3.53	...	...
	2 9	0 8	0.00	- 3.53	...	...
	2 10	2 10	1.21	0.00	0.00	0.00
	2 9	2 9	1.05	0.00	0.00	0.00
	2 7	2 7	0.95	0.00	0.00	0.00
	2 6	2 6	0.95	0.00	0.00	0.00
	2 9	2 10	0.05	0.00	0.00	0.00
	2 6	2 7	0.01	0.00	0.00	0.00
	2 10	2 9	0.05	0.00	0.00	0.00
	2 7	2 6	0.01	0.00	0.00	0.00
	2 9	2 8	0.01	3.53	...	...
	2 7	2 8	0.01	3.53	...	...
	0 8	0 8	0.95	10.73	10.68	-0.05
	0 8	2 7	0.00	14.26	...	...
	0 8	2 9	0.00	14.26	...	...
	0 8	2 8	0.00	17.80	...	...

†The average deviation between measured and calculated splittings is 0.02 Mc while the standard deviation is 0.011 Mc.

*These lines were used to calculate χ_+ and χ_-.

APPENDIX C

QUADRUPOLE INTERACTION SPLITTING FACTOR FOR TWO IDENTICAL NUCLEI OF SPIN 3/2 IN AN ASYMMETRIC ROTOR

APPENDIX C

QUADRUPOLE INTERACTION SPLITTING FACTOR FOR TWO IDENTICAL NUCLEI OF SPIN 3/2 IN AN ASYMMETRIC ROTOR

The tabulation of $\lambda_{\epsilon JF}$ which has been given by Robinson and Cornwell (91) has been extended by the present author to include all values of J up to 40. The calculations were performed on the Burroughs 220 Data-Processing System at the Rich Electronic Computer Center of the Engineering Experiment Station at the Georgia Institute of Technology. This tabulation is presented in Table 13.

Table 13. $\lambda_{\epsilon JF}$ for $J \leq 40$

		J							
ϵ	F	1	2	3	4	5	6	7	8
3	J+3	.50000	.50000	.50000	.50000	.50000	.50000	.50000	.50000
3	J+2	-1.50000	- .75000	-.50000	-.37500	-.30000	-.25000	-.21428	-.18750
3	J+1	- .82287	-1.00000	-.90990	-.83222	-.77627	-.73544	-.70470	-.68085
1	J+1	1.82287	.25000	.10990	.06437	.04294	.03090	.02339	.01835
3	J	*	.00000	-.38309	-.48886	-.52587	-.54018	-.54554	-.54700
1	J	1.00000	.99999	.78309	.70315	.65921	.63109	.61148	.59700
3	J-1	*	1.21824	.44244	.21159	.11897	.07473	.05080	.03660
1	J-1	-2.00000	- .71824	-.54244	-.49731	-.48563	-.48382	-.48487	-.48660
3	J-2	*	*	.90000	.58928	.43333	.34090	.28021	.23750
3	J-3	*	*	1.20000	.98214	.86666	.79545	.74725	.71250
2	J+2	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
2	J+1	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
2	J	1.58113	.93541	.77459	.70076	.65828	.63065	.61124	.59686
0	J	-1.58113	- .93541	-.77459	-.70076	-.65828	-.63065	-.61124	-.59686
2	J-1	*	.00000	.00000	.00000	.00000	.00000	.00000	.00000
2	J-2	*	.00000	.00000	.00000	.00000	.00000	.00000	.00000

* These levels do not exist.

Table 13. $\lambda_{\epsilon JF}$ for $J \leq 40$ (Continued)

		J							
ϵ	F	9	10	11	12	13	14	15	16
3	J+3	.50000	.50000	.50000	.50000	.50000	.50000	.50000	.50000
3	J+2	-.16666	-.15000	-.13636	-.12500	-.11538	-.10714	-.10000	-.09375
3	J+1	-.66187	-.64642	-.63362	-.62285	-.61367	-.60575	-.59886	-.59280
1	J+1	.01481	.01221	.01024	.00872	.00752	.00655	.00575	.00510
3	J	-.54664	-.54544	-.54386	-.54214	-.54040	-.53870	-.53707	-.53554
1	J	.58586	.57702	.56984	.56388	.55886	.55457	.55087	.54763
3	J-1	.02755	.02145	.01716	.01403	.01168	.00988	.00846	.00732
1	J-1	-.48833	-.48988	-.49119	-.49230	-.49322	-.49400	-.49466	-.49522
3	J-2	.20588	.18157	.16233	.14673	.13384	.12301	.11379	.10584
3	J-3	.68627	.66578	.64935	.63586	.62461	.61507	.60689	.59979
2	J+2	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
2	J+1	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
2	J	.58577	.57697	.56980	.56385	.55884	.55456	.55086	.54763
0	J	-.58577	-.57697	-.56980	-.56385	-.55884	-.55456	-.55086	-.54763
2	J-1	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
2	J-2	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000

Table 13. $\lambda_{\epsilon JF}$ for $J \leq 40$ (Continued)

		J							
ϵ	F	17	18	19	20	21	22	23	24
3	J+3	.50000	.50000	.50000	.50000	.50000	.50000	.50000	.50000
3	J+2	-.08823	-.08333	-.07894	-.07500	-.07142	-.06818	-.06521	-.06250
3	J+1	-.58743	-.58265	-.57836	-.57450	-.57099	-.56780	-.56488	-.56220
1	J+1	.00455	.00408	.00368	.00334	.00305	.00279	.00256	.00236
3	J	-.53409	-.53274	-.53147	-.53029	-.52918	-.52814	-.52717	-.52626
1	J	.54479	.54226	.54001	.53798	.53615	.53448	.53297	.53158
3	J-1	.00640	.00564	.00501	.00448	.00403	.00364	.00330	.00302
1	J-1	-.49570	-.49612	-.49647	-.49678	-.49706	-.49730	-.49751	-.49770
3	J-2	.09893	.09285	.08748	.08269	.07839	.07452	.07101	.06781
3	J-3	.59358	.58809	.58321	.57884	.57491	.57135	.56811	.56515
2	J+2	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
2	J+1	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
2	J	.54478	.54226	.54000	.53798	.53614	.53448	.53297	.53158
0	J	-.54478	-.54226	-.54000	-.53798	-.53614	-.53448	-.53297	-.53158
2	J-1	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
2	J-2	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000

Table 13. λ_{cJF} for $J \leq 40$ (Continued)

		J							
ϵ	F	25	26	27	28	29	30	31	32
3	J+3	.50000	.50000	.50000	.50000	.50000	.50000	.50000	.50000
3	J+2	-.06000	-.05769	-.05555	-.05357	-.05172	-.05000	-.04838	-.04687
3	J+1	-.55973	-.55745	-.55534	-.55338	-.55155	-.54984	-.54824	-.54674
1	J+1	.00218	.00202	.00188	.00176	.00164	.00154	.00144	.00136
3	J	-.52540	-.52460	-.52384	-.52313	-.52245	-.52182	-.52121	-.52064
1	J	.53030	.52913	.52804	.52703	.52608	.52521	.52439	.52362
3	J-1	.00276	.00254	.00234	.00217	.00201	.00187	.00175	.00163
1	J-1	-.49786	-.49801	-.49815	-.49827	-.49838	-.49848	-.49857	-.49866
3	J-2	.06489	.06221	.05974	.05746	.05535	.05338	.05156	.04985
3	J-3	.56244	.55995	.55765	.55551	.55353	.55169	.54997	.54836
2	J+2	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
2	J+1	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
2	J	.53030	.52912	.52803	.52702	.52608	.52521	.52439	.52362
0	J	-.53030	-.52912	-.52803	-.52702	-.52608	-.52521	-.52439	-.52362
2	J-1	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
2	J-2	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000

Table 13. $\lambda_{\epsilon JF}$ for $J \leq 40$ (Concluded)

		J							
ϵ	F	33	34	35	36	37	38	39	40
3	J+3	.50000	.50000	.50000	.50000	.50000	.50000	.50000	.50000
3	J+2	-.04545	-.04411	-.04285	-.04166	-.04054	-.03947	-.03846	-.03750
3	J+1	-.54533	-.54401	-.54275	-.54157	-.54045	-.53939	-.53839	-.53743
1	J+1	.00128	.00121	.00114	.00108	.00102	.00097	.00092	.00088
3	J	-.52010	-.51958	-.51909	-.51863	-.51818	-.51776	-.51735	-.51697
1	J	.52290	.52222	.52158	.52098	.52040	.51986	.51935	.51886
3	J-1	.00153	.00144	.00135	.00127	.00120	.00114	.00107	.00102
1	J-1	-.49873	-.49880	-.49887	-.49892	-.49898	-.49903	-.49908	-.49912
3	J-2	.04825	.04675	.04534	.04401	.04276	.04157	.04045	.03939
3	J-3	.54685	.54543	.54409	.54284	.54165	.54052	.53946	.53844
2	J+2	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
2	J+1	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
2	J	.52290	.52222	.52158	.52098	.52040	.51986	.51935	.51886
0	J	-.52290	-.52222	-.52158	-.52098	-.52040	-.51986	-.51935	-.51886
2	J-1	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
2	J-2	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000

APPENDIX D

COEFFICIENTS FOR EVALUATION OF QUADRUPOLE INTERACTION ENERGIES IN ASYMMETRIC ROTOR MOLECULES

APPENDIX D

COEFFICIENTS FOR EVALUATION OF QUADRUPOLE INTERACTION ENERGIES IN ASYMMETRIC ROTOR MOLECULES

The quadrupole interaction coefficients given by Clayton (92) have been extended by the present author to include all states for which the rotational energy has been expressed as a root of a quadratic equation (93). These results are presented in Table 14.

Table 14. Coefficients for Evaluation of Quadrupole Interaction Energies in Asymmetric Rotor Molecules

$J\tau$	$A(J, \tau)$	$B(J, \tau)$
0_0	0	0
1_1	-1/2	1/2
1_0	1	0
1_{-1}	-1/2	-1/2
2_2	$\frac{-\kappa}{(\kappa^2+3)^{\frac{1}{2}}}$	$\frac{1}{(\kappa^2+3)^{\frac{1}{2}}}$
2_1	1/2	1/2
2_0	-1	0
2_{-1}	1/2	-1/2
2_{-2}	$\frac{\kappa}{(\kappa^2+3)^{\frac{1}{2}}}$	$\frac{-1}{(\kappa^2+3)^{\frac{1}{2}}}$
3_3	$-\frac{1}{4}\left[1+\frac{8\kappa-6}{(4\kappa^2-6\kappa+6)^{\frac{1}{2}}}\right]$	$\frac{1}{4}\left[1-\frac{2\kappa-4}{(4\kappa^2-6\kappa+6)^{\frac{1}{2}}}\right]$
3_2	$\frac{1}{2}\left[1-\frac{\kappa}{(\kappa^2+15)^{\frac{1}{2}}}\right]$	$\frac{1}{2}\left[\frac{5}{(\kappa^2+15)^{\frac{1}{2}}}\right]$
3_1	$-\frac{1}{4}\left[1+\frac{8\kappa+6}{(4\kappa^2+6\kappa+6)^{\frac{1}{2}}}\right]$	$-\frac{1}{4}\left[1-\frac{2\kappa+4}{(4\kappa^2+6\kappa+6)^{\frac{1}{2}}}\right]$
3_0	0	0
3_{-1}	$-\frac{1}{4}\left[1-\frac{8\kappa-6}{(4\kappa^2-6\kappa+6)^{\frac{1}{2}}}\right]$	$\frac{1}{4}\left[1+\frac{2\kappa-4}{(4\kappa^2-6\kappa+6)^{\frac{1}{2}}}\right]$
3_{-2}	$\frac{1}{2}\left[1+\frac{\kappa}{(\kappa^2+15)^{\frac{1}{2}}}\right]$	$-\frac{1}{2}\left[\frac{5}{(\kappa^2+15)^{\frac{1}{2}}}\right]$

Table 14. Coefficients for Evaluation of Quadrupole Interaction Energies in Asymmetric Rotor Molecules (Concluded)

$J\tau$	$A(J, \tau)$	$B(J, \tau)$
3_{-3}	$-\frac{1}{4}\left[1 - \frac{8\kappa+6}{(4\kappa^2+6\kappa+6)^{\frac{1}{2}}}\right]$	$-\frac{1}{4}\left[1 + \frac{2\kappa+4}{(4\kappa^2+6\kappa+6)^{\frac{1}{2}}}\right]$
4_3	$\frac{1}{4}\left[1 - \frac{3}{5}\frac{8\kappa-10}{(4\kappa^2-10\kappa+22)^{\frac{1}{2}}}\right]$	$\frac{1}{4}\left[1 - \frac{10\kappa-44}{5(4\kappa^2-10\kappa+22)^{\frac{1}{2}}}\right]$
4_2	$-\frac{1}{2}\left[1 + \frac{27}{5}\frac{\kappa}{(9\kappa^2+7)^{\frac{1}{2}}}\right]$	$\frac{7}{10}\frac{1}{(9\kappa^2+7)^{\frac{1}{2}}}$
4_1	$\frac{1}{4}\left[1 - \frac{3}{5}\frac{8\kappa+10}{(4\kappa^2+10\kappa+22)^{\frac{1}{2}}}\right]$	$-\frac{1}{4}\left[1 - \frac{10\kappa+44}{5(4\kappa^2+10\kappa+22)^{\frac{1}{2}}}\right]$
4_{-1}	$\frac{1}{4}\left[1 + \frac{3}{5}\frac{8\kappa-10}{(4\kappa^2-10\kappa+22)^{\frac{1}{2}}}\right]$	$\frac{1}{4}\left[1 + \frac{10\kappa-44}{5(4\kappa^2-10\kappa+22)^{\frac{1}{2}}}\right]$
4_2	$-\frac{1}{2}\left[1 - \frac{27}{5}\frac{\kappa}{(9\kappa^2+7)^{\frac{1}{2}}}\right]$	$-\frac{7}{10}\frac{1}{(9\kappa^2+7)^{\frac{1}{2}}}$
4_{-3}	$\frac{1}{4}\left[1 + \frac{3}{5}\frac{8\kappa+10}{(4\kappa^2+10\kappa+22)^{\frac{1}{2}}}\right]$	$-\frac{1}{4}\left[1 + \frac{1}{5}\frac{10\kappa+44}{(4\kappa^2+10\kappa+22)^{\frac{1}{2}}}\right]$
5_2	$-\frac{3}{5}\frac{\kappa}{(\kappa^2+3)^{\frac{1}{2}}}$	$\frac{3}{5}\frac{1}{(\kappa^2+3)^{\frac{1}{2}}}$
5_{-2}	$\frac{3}{5}\frac{\kappa}{(\kappa^2+3)^{\frac{1}{2}}}$	$-\frac{3}{5}\frac{1}{(\kappa^2+3)^{\frac{1}{2}}}$

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VITA

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